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ORGANIC GEOCHEMISTRY

ORGANIC GEOCHEMISTRY

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ORGANIC GEOCHEMISTRY

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PREFACE

ORGANIC geochemistry, subject to only the cursory curiosity of most geologists and to the nearly complete neglect of most chemists, has suffered the affliction of passing interest for over fifty years. Many ideas have filtered into the literature that have helped to confuse an already poorly understood borderline science. It is the aim of this volume to present those factual data and ideas that have withstood the test of time and are scientifically sound.

The book has been organized into four parts: (1) a general outline and discussion of principles governing the origin, diagenesis, and classification of organic biochemicals; (2) detailed consideration of major organic deposits; (3) a geochemical review of relatively simple but relatively rare organic substances; and (4) a discussion of the roles played by carbonaceous substances in the geochemical cycles of various elements.

As the treatise developed, it became evident that certain subjects would have to be omitted. Thus, the open literature on the origin and constitution of natural gas was determined to be too sparse to warrant a separate chapter on the subject. Similarly a projected chapter on the organic geochemistry of iron had to be deferred because of a lack of sufficient information to warrant separate treatment of the subject.

No effort has been made to list all the so-called "organic mineraloids" that have been described in the literature. The nomenclature in most instances is confused by local usage, and the substances themselves are generally of minor importance. Descriptions of these substances are already available in works by Dana, Hintze, Doetler, and others.

Selection of the chapters was the sole responsibility of the editor. Contents of the chapters, with the exception of guiding suggestions, however, were left to the discretion of the individual authors. An attempt has been made to avoid duplication, and the volume was also planned to achieve a balanced treatment of the various subjects. Moreover, the fifteen chapters contain hundreds of references for the reader who wishes to extend the treatment of a particular topic. Some attempt has been made to retain reasonable simplicity in the chemical aspects of the work, and geological considerations have been emphasized wherever possible.

IRVING A. BREGER

Washington, D.C.
August 1962

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CHAPTER 1

ORGANIC COSMOCHEMISTRY

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Introduction

THE occurrence of organic substances in stony meteorites has been known for over 100 years (Wöhler and Hörne, 1859). In view of a reawakening of interest in the origin and constitution of such substances, it is appropriate to consider the source of the atoms and fragments that might contribute to the formation of extraterrestrial carbonaceous compounds.

The 5 major constituents of carbonaceous substances are carbon, hydrogen, oxygen, nitrogen, and sulfur. These elements are all of low atomic weight and are thought to be products of low-temperature stellar reactions. They are widely distributed through the cosmos and play major roles in the thermonuclear processes of the stars. Moreover, such isotopes as ${}_6C^{12}$, ${}_8C^{16}$, ${}_{16}S^{32}$ and ${}_{16}S^{36}$ have total proton and neutron numbers divisible by 4 and are particularly abundant.

Carbon, hydrogen, and a number of other elements normally associated with carbonaceous substances have been detected in interstellar space, nebulae, stars, planetary atmospheres, and comets. Table 1 contains a summary of abundances of the first 28 elements of the periodic table as they occur in typical cosmic settings.

It is obvious from Table 1 that meteorites have lost a very high proportion of their lighter elements, presumably through escape because of low gravitational fields. The losses of hydrogen, because of marked volatility of its simpler compounds, and of nitrogen, because of its relatively low chemical affinity, are particularly important with respect to carbonaceous substances.

The tremendous abundances of the elements making up carbonaceous substances, C, H, N, O, and S, in most stars, and in the universe in general, direct one's attention toward their origin and distribution.

Nucleogenesis

The majority of the cosmogonies of the nineteenth and early twentieth centuries were based on the assumption that the most persistent tendencies of organic evolution, as observed in the course of biological and paleontological research, would continue back into the hypothetical set of

TABLE 1

Extraterrestrial Abundances of the Elements

Z	Element	Universe (1) $Si = 10^6$	Atmosphere of τ-Scorpio (2) $Si = 10^6$	Atmosphere of Sun (3, 4) $Si = 10^6$	Interstellar Space (5, 6) atoms/meter^3	Siderites (7, 8) p.p.m.	Chondrites (4, 7, 8, 9, 10) p.p.m.	Achondrites (without metal) (7, 8, 11, 12, 13) p.p.m.
1	*H*	2.50×10^{10}	1.6×10^{10}	5.1×10^{10}	10^6	*Trace*	*Trace*	*Trace*
2	He	3.80×10^{9}	2.8×10^{9}	1.0×10^{10}	—	—	—	—
3	Li	100	—	2.4	—	—	5	—
4	Be	20	—	1.9	—	—	1	—
5	B	24	—	Probably present	—	—	1.5	—
6	*C*	9.3×10^{6}	2.7×10^{6}	1.00×10^{6}	$>0.7–5.2$	*1200*	*1600*	*Trace*
7	*N*	2.4×10^{6}	1.6×10^{7}	2.1×10^{6}	$>0.3–1.8$	*Trace*	*Trace*	*Trace*
8	*O*	2.5×10^{7}	1.6×10^{7}	2.8×10^{8}	*1000*	*Trace*	*323,000*	*429,000*
9	F	1600	—	Probably present	—	—	40	—
10	Ne	8.0×10^{5}	1.8×10^{7}	Absent	—	—	—	—
11	Na	4.38×10^{4}	—	1.0×10^{5}	107	—	7500	5000
12	Mg	9.12×10^{5}	9.3×10^{5}	1.7×10^{6}	—	—	135,500	111,300
13	Al	9.48×10^{4}	5.7×10^{4}	1.1×10^{5}	—	—	14,300	32,500
14	Si	1.00×10^{6}	1.00×10^{6}	1.0×10^{6}	—	—	179,600	232,200
15	P	1.00×10^{4}	—	270	—	180	1500	600
16	*S*	3.75×10^{5}	—	4.3×10^{5}	—	*80*	*20,100*	*5500*
17	Cl	2610	—	Absent	—	—	470	—
18	Ar	1.5×10^{5}	—	Absent	—	—	—	—
19	K	3160	—	8100	10	—	900	2200
20	Ca	4.90×10^{4}	—	8.7×10^{4}	4.7	—	14,300	51,800
21	Sc	28	—	110	—	—	5	—
22	Ti	1680	—	4700	<0.05	—	580	—
23	V	220	—	590	—	—	50	—
24	Cr	7800	—	2×10^{4}	—	—	2700	37
25	Mn	6850	—	1.5×10^{4}	—	—	2400	1800
26	Fe	8.50×10^{4}	7.1×10^{5}	2.7×10^{6}	—	897,000	241,000	125,200
27	Co	1800	—	5500	—	6200	1100	5100
28	Ni	2.74×10^{4}	—	4.7×10^{4}	—	91,000	14,500	74,200

irreversible changes which would have occurred within the primeval universe. Thus, Spencer (1862) claimed that the main trend of "universal evolution" proceeds from a state of more uniform homogeneity, that is, a system of dispersed existencies of relatively simpler internal structure, to a less uniform heterogeneity, involving the formation of more complex individua, be they inanimate or animate. This hypothesis of metaphysics of evolution leads to the conclusion that at an early stage the universe may have consisted of uniformly distributed atoms of hydrogen, which eventually may have evolved from an initial empty space through the intermediate of radiation. Subsequently, the primeval mist condensed into stars in which the heavier atoms were formed. The more complex atoms now in interstellar space are supposed to have been ejected from the stars subsequently through radiation pressure, flare, and nova activity.

The recent paper of Fowler and Greenstein (1956) presents a return to this school of thought in attempting to follow up the synthesis of heavier elements in stars without recourse to an initial dense stage. It is claimed

Notes to Table 1:

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that many stars of relatively higher surface temperature at present synthesize elements up to carbon, and some up to the rare earths.

Most of the theories of the second quarter of the twentieth century, however, disregarded the metaphysical considerations, and attacked the older conclusions on the ground that the pressure and temperature prevailing within a condensing star is inadequate to produce the nuclei in their estimated relative abundances. Thus, a still higher pressure and temperature pre-stellar stage was postulated, which in turn was explained on the basis of the red shift caused by the Doppler effect between nebulae receding from each other (Hubble, 1929). Thus, the conclusion was drawn that the expansion of the cosmos began with the explosive decomposition of an original very dense stage. It is generally agreed by the advocates of the hypothesis of pre-stellar formation of elements that these were generated during a relatively brief period of a few minutes following the "explosion", although views greatly differ as to the character of the original substance or the mechanism of formation of atoms. Theories of formation of the elements through neutron capture by a single or multi-stage expansion of the original neutron-rich medium, or continued creation of matter even after expansion, have also been proposed; a detailed summary of theories of nucleogenesis has been published by Alpher and Herman (1950).

It is difficult to formulate a common denominator for the diverse views regarding the history of matter through the stellar stages. The notion that all the types of stars belong to one or more reasonably well defined evolutional sequences seems to be generally accepted. The evolutional succession of Russell (1925) starts with the red giant stage of incipient star condensation, is followed by the yellow and white giant stars to the gradual concentration of substance, and ultimately to higher temperatures as a result of nuclear reactions. These early stars are characterized by the great predominance of hydrogen lines in their spectra, whereas in the older blue, white and yellow "main succession" stars, spectral indications for heavier elements become progressively more intense. Finally, the white, yellow and red dwarf stars terminate the hypothetical evolutional succession; the latter are the "carbon stars" of spectral types "N" and "P", markedly rich in carbon and its simple groups. Adherents to the hypotheses of pre-stellar formation of the elements hold the view that the gradual emergence of heavier atoms within the surface zones of the stars generating the spectra is not because of their actual synthesis during the successive stages of the hypothetical evolutional sequence, but rather to changes in physicochemical conditions such as the presence or absence of intense convection currents, etc. The variable stars, the novae, or the heavy dwarfs may represent distinct evolutional stages of a single prototype, or may be stages through which only a certain proportion of anomalous stars pass according to the diverse views.

It seems to be generally agreed that the "proton–proton reaction" formulated by Bethe (1939) produces the main energy of the cooler stars gradually converting their hydrogen to helium. The "carbon chain reaction" arrived at independently by Bethe (1939) and von Weizsäcker (1938) is believed to produce the energy of the higher temperature stars, again at the expense of hydrogen which is converted to helium. Many authors until recently felt that, aside from the wholesale formation of He from H, the higher elements are of pre-stellar origin. In the most recent literature, however, there seems to be a partial or entire reversion to the older group of theories attributing to the stars a greater, if not exclusive, role in the formation of heavier elements. Thus, Salpeter in 1953 proposed that, after the gradual exhaustion of H nuclei, the He might polymerize to C^{12}, O^{16}, S^{36}, and other elements.

The considerations of Cameron (1955) are of special interest from the organic point of view as they cast light on the formation of the carbon stars. According to him, following the exhaustion of hydrogen in certain stars, the cores contract and the envelopes expand. Once the cores reach a density of 5×10^4 g/cm^3 and a temperature of 10^8K, the carbon cycle produces neutrons, which will be captured by the surrounding nuclei in relation to their neutron capture cross-sections and original (pre-stellar) cosmic abundances. Therefore, nuclei with 50, 82 and 126 neutrons would concentrate anomalously in the red giant stars. Through further stellar evolution, abnormally high quantities of carbon would form in addition to the heavier elements, thus leading to the carbon stars. Therefore, the carbon stars, which have been placed at the termination of Russell's evolutional sequence (1925), are considered to be anomalous bodies. This hypothesis is supported by the existence of a single higher temperature star (the R.CrB.), which still gives the typical spectrum of the carbon stars.

An extremely thorough treatment of interstellar nucleogenesis, including detailed discussion of the several processes that have been hypothesized as well as proved, has been published by Burbridge, Burbridge, Fowler, and Hoyle (1957). In subsequent papers, Kohman (1961) and Coryell (1961) have developed additional data on the syntheses of nuclei, particularly those of the heavy elements. Cameron (1959) has also contributed in great detail to a discussion of carbon thermonuclear reactions as they enter into the formation of heavier elements. This work is of particular interest to the geochemist concerned with equilibria surrounding the genesis and disappearance of the carbon isotopes.

On the whole, the evidence presented by Burbridge, Burbridge, Fowler, and Hoyle (1957) for interstellar nucleogenesis is most impressive. As noted by these authors, starting with only primeval hydrogen at least 8 synthetic processes are required to explain the cosmic elemental abundance curve (Suess and Urey, 1956). Genesis of the light nuclei takes place in first generation stars where the major elements of carbonaceous substances are formed. Following instabilities in the star and eventual return of the stellar material to interstellar space, stars of later generations are formed. It is in these that the elements of higher atomic weight are synthesized. Although earlier theories of nucleogenesis (Alpher and Herman, 1950; Mayer and Teller, 1949; Klein, Beskow, and Treffenberg, 1946) still have adherents, none explains the origin of the elements in such detail and so elegantly as does that by the Burbridges, Fowler, and Hoyle.

Constituents of Interstellar Space

Atoms exist in interstellar and possibly to a smaller extent in intergalactic space in 3 forms:

(*a*) The atoms can occur singly or combined in groups, the atoms or groups being with or without charge. Among the atoms or groups that are possible, the following have been detected: H, H^+, Na, Na^+, Ca, Ca^+, K, Fe, Ti^+, CH, CH^+, CN, and possibly NaH. The unsaturated character of the atoms or radicals is caused by low pressure and radiation.

(*b*) The atoms can occur in dust particles. The presence of metal, carbon, and silicate particles is inferred from absorption in the red end of stellar spectra.

(*c*) The atoms can also occur in larger solid particles, as evidenced by the occurrence of meteorites.

The total mass of gaseous and solid matter in interstellar space (approx. 3×10^{-26} g/cm^3) has been estimated by Adams (1941) to be of the same order of magnitude as that condensed in the stars. The formation of CH, CH^+, and CN radicals has been explained through chance encounters of the corresponding atoms (Swings, 1942); it has also been argued by Swings and Rosenfeld (1937) that H_2, OH, NH, and CO should also be present by virtue of the great cosmic abundance of these elements.

Stars

Spectroscopic proof has been obtained for the presence of CN, CH, CH_2, and CO groups in the atmospheres of stars having surface temperatures the same as or lower than that of the sun, that is, yellow and red giants, main sequence stars, or dwarfs. Pecker and Peyturaux (1948) found that the CH and CN groups show a quasi-uniform distribution through the disk. In a later paper Pecker (1949) noted a maximum in CH between limb and cafor and still later (Pecker and Athay, 1955), the CH group was detected in the chromosphere of the sun during the eclipse of 1952.

Methane has been identified in the sun (McMath *et al.* 1949) on the basis of absorption bands between 2.15 and 2.45μ in the infrared spectrum. The presence of CH_2 groups in the sun and other stars has been attributed to the following exothermic reaction:

$$2\,CH \leftrightharpoons CH_2 + C$$

Goldberg and Müller (1953) have estimated there to be 1.45×10^{19} molecules of CO per cm^3 on the sun's surface; Goldberg and co-workers (1949) have also presented data for the presence in the sun of $C^{12}O_2^{16}$, $C^{12}O^{16}O^{18}$, and $C^{13}O_2^{16}$. The presence of SiH in the spectra of sunspots and in certain stars reported by Davis (1940) is of some interest as under certain conditions this group may possibly enter organic molecules to form Si—C chains or rings. It should be pointed out, however, that Si—C bonds have not been identified in terrestrial or meteoric carbonaceous substances. The presence of N_2O in the sun has been shown from the 4.06μ absorption in the infrared band (Shaw *et al.* 1950).

Miczaika (1950) noted that red giant stars of high angular velocity show more pronounced CH bands and less marked CN bands than similar stars of low angular velocity.

Feast (1955) has attributed the marked violet opacity of some of the N spectral type carbon stars to depletion of the C_2 molecules through the formation of particles. This may indicate the incipient genesis of carbonaceous substances. An alternate suggestion has been advanced by McKellar and Richardson (1955) who attribute the violet and blue opacity of similar stars to the formation of C_3 molecules. Swings (1954) had earlier suggested that the phenomenon is caused by both dust and C_3 molecules in the stellar atmospheres.

Comets

The existence in comets of groups and radicals made up from C, H, N, and O has been known since the late nineteenth century. In 1943. Swings reported the spectroscopic identification of C_2, CH, CH^+, CH_2, CN, CO, N_2^+, NH, OH, and probably NH_2 and OH^+; at great distances from the sun, however, only CN was detectable. Upon approach of the comet to the sun, the bands of C_2 and CH appear. Near the orbit of Mars CO and N_2^+ show up, and finally inside the orbit of Venus lines of Na and Fe are found for certain comets. The CH and CH_2 groups can be recognized at the perihelion of a fully developed comet. There is incomplete evidence for NH_2 groups near the nucleus, but OH, NH, and CN have been seen near the periphery, and CH^+, CO^+, and NH_2^+ ions occur in the tail.

Schüler (1953) found that spectra produced in the laboratory for C_2H_2, and C_2H_3 resembled the spectra from comets, thus providing evidence for chains of 2 carbon atoms in cometary atmospheres. The presence of NH_3 was inferred on similar grounds by Proisy (1953). Swings later (1956) proposed the existence of C_3 structures from the 4050 Å band in cometary spectra.

It was suggested by Swings (1943) that the molecular fragments identified from their spectra originate through photodissociation of stable molecules that exist within the solid substance of comets. Delsemme and Swings (1952) noted that the relative abundances of CH, CH^+, C_2, CN, NH, NH_2, and OH appear to be approximately equal in cometary atmospheres, whereas the solid, stable molecules, such as CH_4, CO_2, NH_3, etc., from which these may be generated have greatly divergent vapor pressures at the same temperatures. Inasmuch as the hydrates of the compounds have more nearly equal vapor pressures, however, this may be taken as evidence that the parent compounds may have been present as hydrates. It should be noted here that organic molecules of varying complexity may also decompose photochemically or thermally to yield the radicals shown above in nearly equal proportions. The possible existence of C_2 and C_3 compounds within the comet has already been noted. The presence of complex organic substances in carbonaceous chondrites may be related to this suggestion inasmuch as comets could be the parent bodies of these meteorites. The finding of organic sulfur (Mueller, 1953) in solvent extracts from the Cold Bokevelt meteorite thus would also indicate the presence of S_2, SH, etc., in cometary atmospheres.

Planetary Atmospheres

The atmospheres of the inner planets consist principally of oxides or free atoms of C, H, N, O, and S; the outer planets are surrounded by dense atmospheres of the hydrides of these elements. Thus, these elements are primarily in the oxidized state when nearer to the sun, and in the reduced state at greater distances. Because of their higher gravitational fields and lower temperatures, more hydrogen and helium are retained by the outer planets thus providing reducing atmospheres.

There are indications of a very rare atmosphere on Mercury (Phillips, 1936). On Venus, the dense atmosphere consists mainly of CO_2; the failure to detect N_2, O_2, or O_3 indicates that these substances must be present in small percentages compared to the Earth's atmosphere (Adams, 1932). There have been recent reports of the detection of H_2O in the atmosphere of Venus. In order to explain the dense clouds at prevailing temperatures of over 50°C, Wildt (1940) proposed that photochemical reactions may partly dissociate the CO_2 into CO and O; that formaldehyde may form through the following reaction;

$$H_2O + CO_2 \xrightarrow{h\nu} HCHO + O_2$$

and the formaldehyde so generated would polymerize to (CH_2O) polymers which would form the clouds. As later ultraviolet spectral analyses failed to detect formaldehyde, the theory was withdrawn, although it was noted that the negative result may be due to the fast rate of polymerization of the formaldehyde (Wildt, 1942).

The atmosphere of the Earth differs, on the whole, from those of the other 2 inner planets by its marked richness of N_2, O_2 and H_2O at the expense of CO_2.

The atmosphere of Mars has been reported to contain about 20% CO_2; other constituents could not be identified as their pressure is less than one fifth that of the terrestrial atmosphere. However, N_2, with subordinate quantities of H_2O, CH_4, NH_3, NO, O_2, O_3, and inert gases were inferred. According to Rosen (1953), the violet haze is not caused by H_2O or CO_2 crystals, as formerly believed, but to carbon smoke. The clouds and the white material collecting on the polar areas during the respective winters are believed to be ice or solid CO_2. The temperature has been thought to be too high for the condensation of CO_2, however, and it has been calculated that a partial vapor pressure as little as 0.5 mm would be sufficient to produce the clouds and the precipitation of the ice crystals during the polar winters (Hess, 1948).

The asteroids lack atmospheres because of their small sizes.

The atmospheres of the 4 outer planets show, on the whole, marked uniformity in contrast to those of the inner planets. According to Adel and Slipher (1934), the CH_4 pressure on Jupiter is 800 Mile-Atm; Dunham estimated the NH_3 pressure to be 10 Mile-Atm (1939). These authors have also reported the CH_4 pressure on Saturn to be 800 Mile-Atm, and have noted that NH_3 has a lower partial pressure on Saturn because it would tend to condense at the lower temperatures. The atmospheres of Uranus and Neptune contain no NH_3 for the same reason. Herzberg (1952) observed bands of H_2, partially masked by those of CH_4 in the atmospheres of the latter 2 planets. The intensity of these proved to be closely comparable with those originating from a laboratory mixture of 3 parts of He and one part of H_2 at a partial pressure of 2 atm and at 78°K.

It has been argued that, owing to the marked H_2 saturation in the atmospheres of the outer planets, higher hydrocarbons would not polymerize from the original mixture consisting of H_2, CH_4, NH_3, and CO_2 (Russell, 1935). This consideration was supported by Adel and Slipher (1935) who could identify no appreciable amounts of C_2H_6, C_2H_4, or C_2H_2 in the atmospheres of Uranus and Neptune. Although these gases condense at lower temperatures than NH_3.

An atmosphere of CH_4 on Titan, the largest satellite of Saturn, has been spectroscopically proved (Kuiper, 1944). As the gravitational field of Titan is lower than the escape threshold of hydrogen, conditions there seem to be more favorable for the photochemical condensation of higher molecular organic substances than in the case of the H_2-saturated outer planets. For this reason, a thorough spectroscopic examination, so far as experimental conditions permit, of the atmosphere of Titan for traces of two-carbon molecules may prove to be of considerable theoretical interest.

A summary of data regarding the extraterrestrial occurrence of atoms normally associated with carbonaceous substances is shown in Table 2. A few groups of interest have been included in the table even though they have not been discussed in the text.

Meteorites

Inasmuch as the only extraterrestrial carbonaceous substances that are available for study have arrived on meteorites, a short review of the nature of meteorites is appropriate.

It has been estimated that between 1000 and 10,000 tons of meteoritic material fall on Earth daily. Most meteorites are small, and only a few are spectacular in size. Larger falls are accompanied by much noise and light,

TABLE 2

Extraterrestrial Molecules and Groups of the Major Elements Related to Carbonaceous Substances

	Spectroscopic Evidence		
Source	Conclusive	Inconclusive	Inferred
Interstellar Space	$H > O > CH > CN$	(C particles)	H_2, O_2, CO, NH, OH
Red giant stars	H_2, CH, CH_2, CN, CO	—	—
Sun	H_2, N_2, O_2, S_2, CH, CH_2, CH_4, CN, CO, CO_2, N_2O, SiH	PH	—
Carbon Stars	H_2, CH, CH_2, CN, CO	C_2, C_3, NaH	—
Comets	C_2, N_2^+, CH, CH^+, CH_2, CN, CO^+, NH, OH	C_2H, C_2H_2, C_2H_3, NH_2, NH_3, OH^+	CS, SH, S_2
Tails of comets	CH^+, CO^+, N_2^+	—	—
Venus	CO_2, H_2O	—	N_2, O_2, O_3, CO, HCHO, H_2O
Mars	CO_2	H_2O (C particles)	N_2, O_2, O_3, CH_4, NH_3, NO
Jupiter and Saturn	$CH_4 > NH_3$	—	H_2, N_2
Uranus and Neptune	CH_4	H_2	N_2
Titan	CH_4	—	C_2H_6, C_2H_4, C_2H_2

the luminosity being that of the compressed air in front of the meteorite where kinetic energy is converted into heat. The surface of the meteorite usually melts and emits glowing particles that produce a glowing tail and a trail of smoke. The heat is produced only over a period of a few seconds, and has no time to penetrate to the interior of the body, which remains at the temperature of outer space. Conduction of heat to the interior of a meteorite is dependent upon its size and composition. Iron meteorites will, thus, heat up faster than stony meteorites. Meteorites are commonly named after their place of fall, others are identified by craters.

Various classes of meteorites are known and their constituent minerals have been studied in detail.

Siderites, or Irons, contain an average of 98% metal and consist mainly of nickel and iron in 2 major mineral species: Kamacite which is α-iron, body-centered, and contains 5–8% nickel; and taenite, which is face-centered γ-iron containing 25–50% nickel. Small amounts of cobalt are always present in the siderites. Other accessory minerals are schreibersite (Fe, Ni) P_3, and oldhamite (CaS), both of which are known only in meteorites because they hydrolyze readily; troilite (FeS), cohenite (Fe_3C), and graphite (C). Cohenite is very abundant in all siderites.

Stony-irons, siderolites, or pallasites are rare, have no fixed composition, and consist of about equal quantities of metallic and silicate phases. The silicate is usually olivine, and troilite is commonly present.

The stones, or aerolites, have been sub-divided into 2 major categories, the chondrites and achondrites.

About 90% of stony meteorites contain spherules, of microscopic size or identifiable by eye, which are called chondrules. These are usually olivine, (Mg, Fe) Si_2O_4, or enstatite, $MgSiO_3$, imbedded in a groundmass of similar material. These chondrule-containing meteorites are called chondrites.

The average composition of chondrites is:

12%	nickel and iron
46%	olivine
21%	hypersthene
4%	diopside
11%	plagioclase.

Stony meteorites without chondritic structure are called achondrites and have the following average composition:

1%	nickel and iron
9%	olivine
50%	hypersthene
12%	diopside
25%	plagioclase.

The stony meteorites occasionally contain carbonaceous substances which will be discussed in detail in a later paper of this chapter.

Tektites are small glass-like meteorites containing, as a rule, more silica than obsidian or most acid igneous rocks.

Numerous hypotheses have been proposed to explain the origin of meteorites. Although it is generally agreed that meteorites are fragments of celestial bodies, there is no real agreement as to the size of the bodies from which they were derived. An original Earth-size body has been postulated on the basis of equilibrium conditions that would account for the differentiation of iron–nickel and silicate phases (Brown and Patterson, 1948). On the other hand, Urey and Craig (1953) suggested smaller bodies, possibly asteroids, as the source bodies of meteorites. It was hypothesized that the majority of the meteorites originated from 2 asteroids that collided causing the formation of globules of fused silicates, which subsequently solidified to chondri.

The fact that most of the meteorites strike the Earth in a general east–west direction seems to indicate that the majority of them originate from parent bodies, asteroids or comets, of the Solar System. After careful revision of equilibrium conditions between the iron and silicate phases, and taking into account other factors, Lovering (1957) proposed a volume approaching that of the Moon for the parent body of the meteorites.

Although there are differences of opinion on the size of the parent body or bodies that have given rise to meteorites, the accumulation of these bodies from the solar nebula is generally thought to have occurred at temperatures below 600°K. A detailed discussion of the origin of meteorites, with many pertinent references, was recently published by Anders and Goles (1961).

Isotopic Composition of Extraterrestrial C, H, N, O, and S

Isotope ratios of the above elements are of considerable theoretical interest because they can at times be interpreted as geological indicators of physicochemical conditions that prevail in a given setting. More important, perhaps, is the fact that such ratios may furnish evidence as to the biological or non-biogenic origin of given organic substances. The following summary for 5 elements can be amplified by reference to the paper of Ingerson (1953) and to Rankama's book (1954).

Carbon—Cosmic variations of the C^{12}/C^{13} ratio are higher than similar variations for other elements. The lower limit of the C^{12}/C^{13} ratio in giant stars of spectral types G8 to K1 ranges from 23 to 7; those in classes K2–K5 have C^{12}/C^{13} equal to 15–0.6 (Schopp, 1954). By spectroscopic examination of the bands for CN, C_2, etc., of 21 R-type carbon stars, McKellar (1949) found that 3 showed maximum values for C^{12}/C^{13} of 70, 60, and 30; in 6 stars the bands were too strong for quantitative measurements; 12 gave values close to 3.4, and one gave a transitional value of 4.8. The 25 N-type stars examined all showed much C^{13}. The sun belongs to the high C^{12}/C^{13} group of stars as its ratio for C^{12}/C^{13} exceeds 36 (Greenstein *et al.* 1950). The high C^{12}/C^{13} ratio seems to be characteristic for the entire solar system. As an example, it has been found that the C^{12}/C^{13} ratio of the CO_2

atmosphere of Venus is similar to that for terrestrial carbon, i.e. about 90 (Kuiper, 1952).

Swings (1943) concluded that the Halley and Brooks comets of 1910 and 1911 contained markedly lower C^{12}/C^{13} ratios than the mean for the solar system or Earth, whereas the comet 1940c contained little C^{13}. It is interesting to note that the high angle between the orbit of the Halley comet and the plain of ecliptic (162° 13′) indicates that this celestial body, with an anomalously low C^{12}/C^{13} ratio, is not an original member of the solar system.

The marked diversity of cosmic C^{12}/C^{13} ratios is explicable through reference to the carbon cycle which sets in when the necessary critical temperature and pressure conditions are met. The reactions, independently proposed by von Weizsäcker (1938) and Bethe (1939) are as follows:

$$C^{12}\ (p,\ \alpha)\ N^{13}\ (\beta^{+}V_{+})\ C^{13}$$
$$C^{13}\ (p,\ \alpha)\ N^{14}$$
$$N^{14}\ (p,\ \alpha)\ O^{15}\ (\beta^{+}V_{+})\ N^{15}$$
$$N^{15}\ (p,\ \alpha)\ C^{12}$$

These reactions occur when C^{12} is mixed with H^{1} at high enough temperatures, and He^{4} is synthesized from the H^{1} by means of the CN cycle. The reactions produce C^{13} and 2 stable isotopes of nitrogen, N^{14} and N^{15}.

Opinions differ as to which C^{12}/C^{13} ratio represents the original relative abundances of the isotopes. Some have claimed that equilibrium in the carbon cycle has not yet been attained in the majority of the stars, those having the high C^{12}/C^{13} ratios (Shain and Gaze, 1952). The same workers feel that the minority of the stars, those with low C^{12}/C^{13} ratios, represent the post-carbon-cycle state of the element. Similar views were expressed by McKellar in 1950, but in an earlier paper this same author (1949) claimed that the giant stars all show low C^{12}/C^{13} ratios and that a value of 3 should best represent the original C^{12}/C^{13} ratio.

Measurement of widths of the CH and CH^{+} bands from interstellar space and clouds has led to the conclusion that the C^{12}/C^{13} value is approximately 5 (Wilson, 1948). Urey (1951) has also suggested that the C^{12}/C^{13} ratio for terrestrial carbon, approximately 90, indicates that it may have passed through the carbon cycle. As interstellar space and apparently pre-stellar nebulae may contain more pre- than post-carbon-cycle carbon, a low ratio for original carbon is indicated.

Each star may have its own particular C^{12}/C^{13} ratio and local variations are also to be expected. Thus, C—C, C—O, and C—N bonds have been found to break more readily between C^{12} atoms than between C^{13} and C^{12} atoms. Also, on fractionation of a molecular mixture where the molecules are of identical sizes, those richer in C^{13} tend to concentrate in the residue.

Both of these factors would tend to concentrate C^{13} in the relatively high molecular weight substances in nature, such as residues from distillation or fractionation, or gravitational differentiates of higher density. On the other hand, organisms on Earth produce complex molecules preferentially using C^{12}, and tend to eliminate a relatively high proportion of C^{13} in simple metabolic products such as urea, CO_2, etc. In this respect it has been experimentally noted that oxidized compounds tend to concentrate C^{13}, and reduced compounds tend to concentrate C^{12} (Craig, 1953).

From the above it is clear that the C^{12}/C^{13} ratios in stars are not only very large but vary over a wide range. On Earth, however, where biochemical processes rework the initial isotopes, there is a tendency for reduced and oxidized products to attain an equilibrium only slightly disturbed by possible photochemical or local metamorphic reactions.

It may be anticipated that low-molecular-weight substances on Earth that originate in biochemical processes, such as gas or petroleum, should represent the differentiate of highest C^{12}/C^{13} ratio, and that this is to be followed by essentially undifferentiated biogenic sediments, such as the coals and graphites. On the other end of the scale, sedimentary carbonates, containing the reworked CO_2 of the organisms, should show the lowest values. Carbon of presumed purely or mainly magmatic origin, such as occurs in diamonds, pegmatitic graphites, or magmatic carbonatites, should be of intermediate isotopic composition.

TABLE 3

Carbon Isotope Ratios for Meteorites

Type	Murphy, 1941		Trofimov, 1950	
	No. of analyses	C^{12}/C^{13} Range	No. of analyses	C^{12}/C^{13} Range
Siderites	3	89.8–91.6	10	89.6–91.2
Stony-irons	3	91.1–92.0	3	90.6–91.8
Stones	1	91.7	23	89.6–91.2
Carbonaceous chondrites	—	—	3	89.9–90.9

As carbonaceous substances on Earth have had, as a rule, complex histories, degrees of overlap in isotope ratios among different types are to be expected. As an example, marine organisms were found to be of isotopic composition intermediate between the 2 main biological differentiates as their bodies contain both organic and carbonate carbon.

Very considerable differences in carbon isotope ratios have been found for sedimentary carbonates of different geological ages (Jeffery *et al.* 1955). It was observed that the C^{12}/C^{13} ratio is markedly low in Devonian limestones, high in Miocene limestones, and intermediate in those of Cambrian age. These differences were attributed to possible periodic liberation of much juvenile CO_2 through volcanic activity.

The C^{12}/C^{13} ratios of meteorites are very close to the apparent mean values for the solar system as shown in Table 3 (Murphy, 1941; Trofimov, 1950).

Boato (1954) reported that the C^{12}/C^{13} ratio increases with increasing total carbon content, but this observation is not borne out by the data of Table 3.

The C^{12}/C^{13} ratio of graphite from the Cañon Diablo meteorite was found to be 89.45, whereas the ratio for the carbon from associated cohenite, $(FeNi)_3C$, from the same sample was 90.51 (Craig, 1953). These appear to be the only data for C^{12}/C^{13} ratios for different phases of the same meteorite. Comparisons between the ratios for solvent-extractable and non-extractable organic substances of carbonaceous chondrites may provide information regarding the unity or diversity of the histories of the substances.

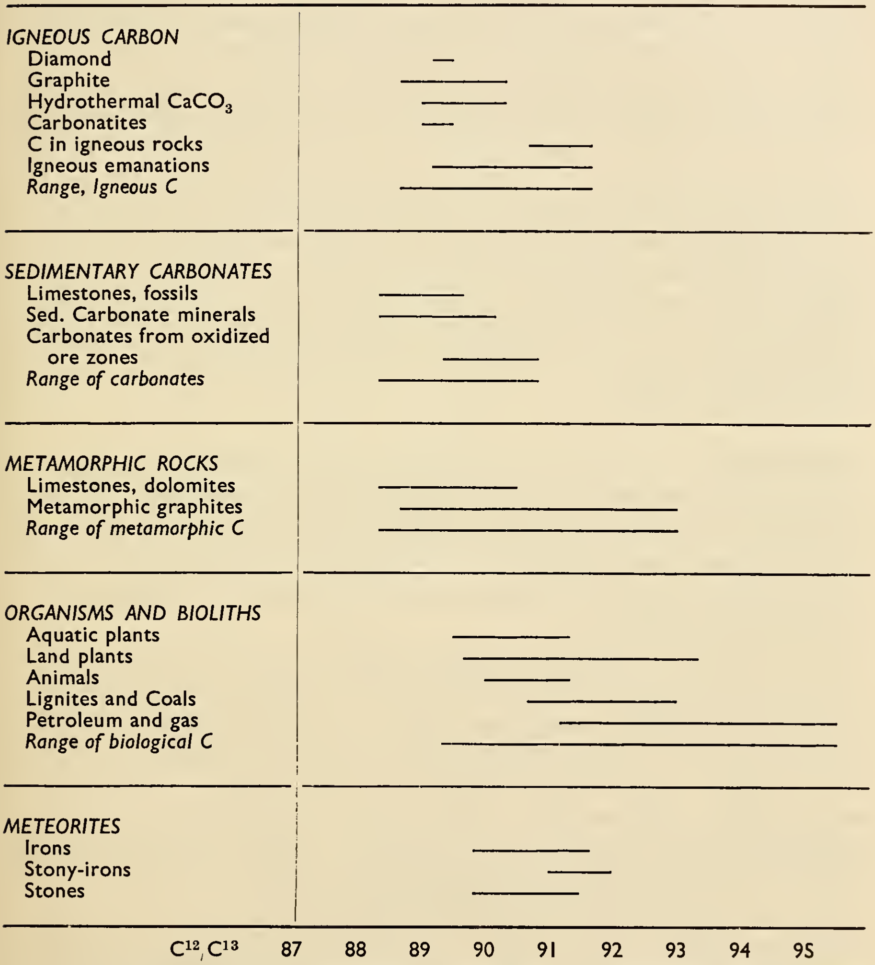


FIG. 1. Comparison of C^{12}/C^{13} ranges for meteorites with those of the main types of terrestrial carbon.

It is apparent from Fig. 1 that the C^{12}/C^{13} range of carbon from meteorites is rather closely comparable, although somewhat higher, than that of presumably little differentiated, non-biogenic, juvenile carbon of magmatic origin in the earth's crust. The rather great spread of values for limestones on the one extreme and for petroleum and natural gas on the other is significant in indicating a non-biological origin of carbon from all types of meteorites thus far examined.

Nothing is known regarding the C^{14} content of meteorites. This isotope is formed from N^{14} through cosmic irradiation in the earth's atmosphere, and subsequently is assimilated by plants from atmospheric CO_2. The method of C^{14} age determinations through the gradual decay of the radioisotope, after its absorption by living organisms and following their death, has an extensive literature. Nitrogen and some of its simpler compounds have been liberated from meteorites upon heating; organic extracts from the Cold Bokevelt carbonaceous chondrite have also been found to contain considerable amounts of the element (Mueller, 1953). It should be anticipated, therefore, particularly in the case of carbonaceous chondrites, that C^{14} should be present. From the N^{14}/C^{14} ratio, the intensity of the cosmic radiation within the space traversed by the meteorite during the last few thousand years could be estimated. In the case of "finds", the approximate date of the "fall" could also be assessed through comparison with meteorites of known date of fall. The results obtained could subsequently be compared with those used to estimate total intensity of cosmic radiation through the amount of He^3 generated. These potential uses of meteorites as "integrating cosmic ray meters" are discussed by Singer in 3 papers (1952, 1953, and 1957).

Hydrogen—The 2 stable isotopes of hydrogen, protium and deuterium, appear to be more uniformly distributed throughout the cosmos than those of carbon. Thus, Gauzit (1952) concluded that the H^1/H^2 ratio of the sun cannot be lower than that on Earth. Also, Swings (1943) could not observe an abnormally high H^1/H^2 ratio in any of the comets for which spectroscopic data are available.

The terrestrial deuterium content seems to be mainly governed by distillation processes. Thus, it is generally low in fumarole vapors (down to 0.0079 mole % H^2), and rather high in the oceans, reaching the value of 0.0156 mole %. There is no conclusive evidence as yet of biochemical differentiation of hydrogen isotopes, but even if this proved to be the case, the effect could easily be masked by the far more important factor of fractionation. Also, biochemical fractionation would be difficult to assess because of the great mobility of hydrogen.

As a rule, hydrogen in meteorites conforms to terrestrial H/D ratios (Friedman, 1953). An increase in the deuterium content of hydrogen liberated at progressively higher temperatures from the Cañon Diablo meteorite has been noted, but Friedman recommended caution in interpretation of the results because of possible exchange of hydrogen with that from terrestrial water. Similarly, it has been noted that the H/D ratio of water from carbonaceous chondrites falls within that for terrestrial substances and is similar to that for hydrogen liberated from siderites (Edwards, 1955). The suggestion made by Edwards that the H/D ratio of the carbonaceous chondrites represents the primeval isotopic composition of hydrogen was refuted by Boato (1956) on the grounds that, according to present theories of ultimate genesis of meteorites, their parent bodies may have been subjected to processes as distillation, etc. Reference was also made to the very considerable loss of water when the stones were placed in a vacuum.

In this connection it should be noted that the weight of the Orgeuil carbonaceous chondrite varies directly with humidity and inversely with temperature (Mueller, unpublished data). Powdered samples showed a diurnal fluctuation in weight of as much as 3.45% when kept in the open, and 1.03% in a normal laboratory room; a specimen within a museum showcase varied by 0.28%. These values were based on minimum weights of the samples during 5 days of observation; the samples containing approximately 25% water.

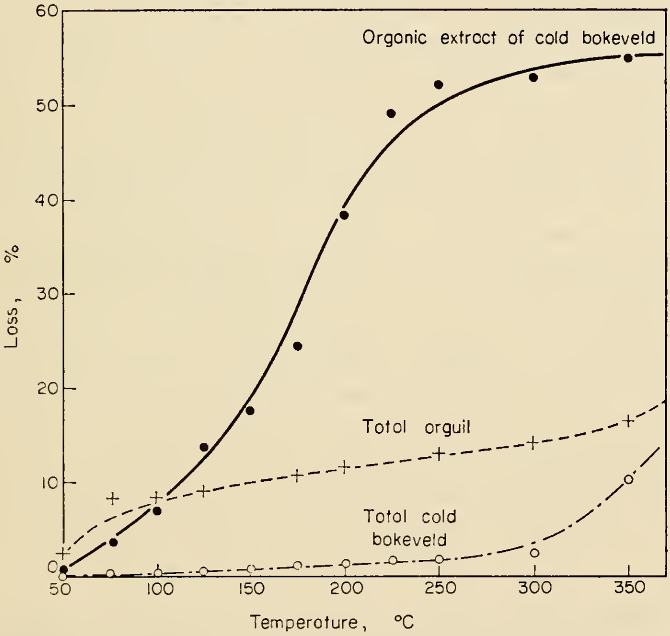


FIG. 2. The low temperature thermal decomposition of the Cold Bokeveld and Orgeuil carbonaceous chondrites.

The marked decomposition of this particular meteorite at temperatures below 100°C (see Fig. 2) seems to indicate that it contains abnormally high quantities of hygroscopic substances. This is particularly important because each year over 3 times the total water content of the chondrite is involved, even under "showcase" conditions.

Prior to interpretation of H/D determinations it is necessary to determine how repeated diurnal exchanges of the rather loosely held water effect the hydrogen more firmly bound in the carbonaceous or hydrated silicate phases. Samples of the meteorite could be maintained in an atmosphere of D_2O vapor in which the diurnal (and seasonal) changes of humidity, temperature, and pressure could be reconstructed. Subsequently, the deuterium content of the water and hydrocarbon fractions liberated at higher temperatures could be compared with those from untreated samples. If the above procedure indicated that very little or none of the more intimately associated hydrogen exchanges during the average terrestrial history of a given meteorite, only then would comparison of the H/D ratios of the hydrated silicates and organic extracts yield significant data.

Nitrogen—Little is known regarding the isotopic composition of nitrogen in stars, although there are indications that the N^{15} isotope may be enriched in the carbon stars at the expense of N^{14} (Swings, 1948).

The isotopic composition of nitrogen in meteorites is unknown. The determination of the isotopic ratios from nitrogen-containing compounds released on heating the meteorites, or from the more abundant nitrogen obtained from the organic compounds of the carbonaceous chondrites may provide indications as to the possible conditions that prevailed on the parent body. Thus, the increase of the N^{14}/N^{15} ratio from 273 at the earth's surface to 282.6 at a height-range of 54.7 to 58.3 kms was observed in samples of air obtained from rockets, indicating a gravitational segregation of the isotopes (McQueen, 1950). On the other hand, it was found that the N^{14}/N^{15} ratio tends to decrease with increasing geological age of terrestrial rocks, possibly because of preferential diffusion of the lighter isotope (Mayne, 1957). The combination of factors leading to changes in the isotopic composition of nitrogen within different celestial bodies, and the telescoping of effects of gravitational field and age, may render the interpretation of meteoritic isotopic composition of nitrogen difficult and not without considerable ambiguity. More positive information could, however, be obtained through comparison of the isotopic ratios in different meteorites; similarity of these would indicate that the samples investigated originated from either the same body or from objects with similar histories.

The biological fractionation of nitrogen seems to be insignificant in relation to the factors outlined above. For this reason, it is unlikely that nitrogen isotope ratios could furnish reliable data as to the absence or presence of living organisms on the parent bodies of the meteorites.

Oxygen—There is no conclusive evidence for any marked changes in isotopic composition of oxygen throughout the universe; by and large, the 3 stable isotopes of the element, O^{16}, O^{17}, and O^{18}, are evenly distributed. Oxygen fractionates in the Earth's atmosphere and crust through numerous processes in close parallelism with hydrogen. The role of the living organism in the fractionation of the isotopes has still not been established but, in any case, it would be masked by the stronger effects of fractionation by non-biological processes.

The O^{16}/O^{18} ratios of stony meteorites fall, on the whole, within the range of terrestrial subsilicic igneous rocks, namely, 160–180; the ratios for tektites are lower (Silverman, 1951). No information is as yet available as to the O^{16}/O^{18} ratio of the organic phase of the carbonaceous chondrites.

Sulfur—The isotopic composition of sulfur in the stars is as yet unknown. The four stable isotopes, S^{32}, S^{33}, S^{34}, and S^{36}, show marked fractionation in nature and, as a rule, the proportion of each of the 3 heavier isotopes to the lightest one tends to increase or decrease in the same manner. For this reason, the S^{32}/S^{36} ratio can be considered characteristic and is usually the only one determined. The S^{32}/S^{36} ratio is highest in biogenic sulfurs with observed values up to 23.00, and is lowest in sulfurs of sedimentary origin with values as low as 21.60. These 2 types of sulfur appear to be more or less biogenic differentiates: in the former the sulfur is concentrated in the living frames of organisms, and in the latter, analogous to the differentiation of carbon isotopes, the sulfur is eliminated in low molecular weight substances during metabolic processes. Again, in analogy with carbon, sulfur of juvenile magmatic origin is apparently of intermediate isotopic composition. The differentiation of sulfur isotopes in the geochemical cycle has been discussed in considerable detail by Sakai (1957).

The sharp biological differentiation of sulfur isotopes should make sulfur an important "biological indicator" in establishing the ultimate origin of the organic substances in meteorites. The isotopic composition of sulfur in the troilite (FeS) of siderites lies within the range of terrestrial fumarolic and other juvenile types of sulfur indicating a non-differentiated state (MacNamara and Thode, 1950; Trofimov, 1949). Isotopic analyses of sulfur from oldhamite, (CaMn) S, daubreeite ($FeCr_2S_4$), and the sulfate phases of stony meteorites, and in particular the free sulfur extractable with carbon disulfide and the organic sulfur of carbonaceous chondrites, could be of particular importance in organic geochemistry.

Conclusions—Much information can be gained relevant to the origin of the carbonaceous phase of meteorites, and relevant to meteorites in general, through the following 2 types of studies: (1) Comparison of isotopic ratios from the major elements of the carbonaceous phase with those from Earth; (2) Comparison of isotopic ratios from the same phase of different meteorites. Carbon and sulfur appear to hold most promise for such study because they undergo appreciable differentiation during biological processes.

The effects of biological differentiation of nitrogen and oxygen appear to be of relatively secondary importance, and the value of hydrogen isotope ratios requires experimental confirmation.

Properties of the Carbonaceous Phase of Meteorites

Cohen, in 1894, published a summary of studies on carbonaceous meteorites that were carried out between 1835 and 1885. Claims had been made that organic substances were extracted with ether or alcohol from the following stones: Allais, Cold Bokevelt, Collescipoli, Kaba, Meghei, and Nagaya. Furthermore, the Orgeuil and Goalpara meteorites were reported to yield carbonaceous residues after removal of inorganic matter. Thirteen other stones were said to contain carbonaceous substances on less positive grounds, such as dark grey color, odor on heating, etc. All the meteorites were said to be chondrites except Goalpara which, according to Tschermak (1870), is an achondrite of chondritic composition. In 1954, Boato examined 13 of the carbonaceous chondrites and subdivided them, on the basis of water and carbon content, into the following 2 groups:

(A) H_2O, 1.7–4.7%; C, 1.5–3.3%
(B) H_2O, 0.2–0.8%; C, 0.4–0.8%.

The existence of 2 such distinct groups, however, seems to be somewhat doubtful in view of the diversity of composition within each of the 2 groups and the small number of stones examined. It has still not been established whether there is a continuous transition in organic matter content between the carbonaceous chondrites and other chondrites, or if the organic material disappears abruptly in going from one group to the other. This uncertainty is based on the fact that investigational methods of the nineteenth century could not, as a rule, detect under 0.5% organic matter, which appears to be the content of the "poorest" carbonaceous chondrites thus far reported. A systematic organic chemical examination of the stony meteorites may reveal a detailed distributional pattern of organic substances together with their variability. In this connection, the study of the stones belonging to the "grey chondrite" class of the Rose–Tschermak classification may be of particular interest, as the color, texture, and petrographic properties of these seem to be transitional towards the carbonaceous chondrites. Comparison of the percentages and properties of the organic phase from various stones of the same shower may also yield interesting data, if such samples are available.

With regard to inorganic constituents, the compositions of carbonaceous chondrites lie, on the whole, within the range of the rest of the chondrites. Urey and Craig (1953) rejected all the nineteenth century organic analyses of the Cold Bokevelt, Felix, Indarch, Kaba, Nagaya, Orgeuil, and Staraya Boroskino carbonaceous chondrites as being unreliable because of diverse inconsistencies. The conclusion was reached, however, that these meteorites belong to neither the "high" or "low" iron classes distinguished by these authors. Recent analytical data by Wiik (see Boato, 1956) indicate that the composition of the carbonaceous chondrites lies not only within the general range of chondrites, but actually coincides, on the basis of total iron and its distribution between the silicate and metal phases, to the "high" class.

Analyses for Na and K have been carried out on the following carbonaceous chondrites by Edwards and Urey (1955): Cold Bokevelt, Felix, Haripura, Ivuna, Meghei, Mokoia, Murray, and Orgeuil. It was found that the Na/K ratio is close to 10 with the exception of a low value for the Murray, and is somewhat higher than the value of 8 for the rest of the non-carbonaceous chondrites analyzed. The Si/Alkali ratio was also found to be more variable in the carbonaceous chondrites. Comparison of minor and trace element composition of the Meghei carbonaceous chondrite with the Homestead chondrite led Pinson (1954) to conclude that they fall within the same ranges in the two meteorites. One exception noted was that the carbonaceous meteorite has less Li, Na, K, and Rb by factors varying between 5 and 8.

As has already been noted, all carbonaceous chondrites contain appreciable percentages of water. Zavaritskii and Kvasha (1952) found that the Staraya Boroskino stone lost 2.96% water below 105°C and 8.72% above that temperature. Similarly, the Meghei meteorite lost 2.15% water below 105°C and 8.35% above 105°C. In attempting to establish the origin of the water, they were able to separate chlorite, $n = 1.589–1.625$, and $n = 1.570$ from the 2 samples, respectively, and claimed that, although their dehydration curves differ, they both resemble those of chlorites. That the bulk of the thermally liberated water is bound to originate in hydrated silicates, and only a small proportion from the decomposition of the carbonaceous complex, is evident on inspection of the H_2O/C ratios shown above for Boato's (A) and (B) chondrite groups (1954). When the Cold Bokevelt meteorite was heated to 500°C it underwent a loss of weight of 16.81%, most of which was water (Mueller, 1953). Of this loss of weight only 2.15% could be regained by permitting the sample to stand 250 days in a water-saturated atmosphere at room temperature. This irreversibility of water absorption following rather moderate heating indicates that at least an appreciable proportion of the water must be an original constituent of the stone. On the other hand, the great diurnal variation of water content observed by the author in the case of the Orgeuil meteorite illustrates the difficulties of assessing the percentage of water within the original substance in outer space. Values obtained after treatment in vacuum may well be too low, however, as the substance was at an unknown, but presumably very low, temperature in space.

It is well known that all meteorites, especially the carbonaceous chondrites, liberate gas when heated. Zavaritskii and Kvasha (1952) reported that H_2O, CO_2, CO, CH_4, H_2, and N_2 are liberated when carbonaceous chondrites are heated. In addition, Buddhue (1942) claimed identification of cyanogen, $(CN)_2$ and NH_3. During distillation of the Cold Bokevelt meteorite, aqueous emulsions containing 0.25% sulfur and a trace of brown to black carbonaceous substances were formed (Mueller, 1953). The gases released during this work were inflammable and, judging from their odor, contained higher organic molecules. Because of the small quantity of meteorite available for this work no definite substances could be identified.

References in Cohen's book (1894) indicated the organic extracts from the meteorites to be yellow resins of soft consistency. Exceptions to this generality were reported for the Kaba stone by Wöhler (1859), who described the extract to be of waxy consistency. This may indicate that the extracts from most of the chondrites consist of rather complex oxygen-, nitrogen-, and sulfur-substituted, and possibly unsaturated, molecules, whereas that from the Kaba stone may be more paraffinic in nature. In this respect it is interesting to note that of 18 carbonaceous chondrites examined for fluorescence, only the surface crust of the Kaba stone showed a faint brown diffuse glow (Mueller, 1953). From experiences with terrestrial bitumens, this is known to be characteristic for substances relatively rich in paraffinic molecules or in those structures having high H/C ratios.

Microscopic examination of thin sections of the Cold Bokevelt meteorite have shown the carbonaceous phase to be finely divided and disseminated within the groundmass of the stone (Mueller, 1953). Use of methyl alcohol, ethyl alcohol, chloroform, benzene, and carbon disulfide, in that order, led to total extraction of 1.12% by weight of organic material; application of the solvents in the reverse order, omitting carbon disulfide, led to extraction of 1.13% by weight of the meteorite. Water extracted nothing from the meteorite, and none of the extracts exhibited measurable optical rotation.

TABLE 4

Organic Microanalysis of Extracts from Cold Bokevelt Meteorite

Element	In organic extract	Total in meteorite	Percentage of total in organic extract
	%	%	
C	19.84	2.20	10.09
H	6.64	1.53	4.87
N	3.18	<0.05	70.0
S	7.18	1.99	4.04
O (By diff.)	40.0	35.84	1.25
Cl	4.81	Not determined	?
Ash	18.33	—	—

The extracts had a "spicy" odor, were soluble in all the solvents, were not attacked by acids, and dissolved in alkali with precipitation of some iron oxide. Organic microanalysis of the extracts are shown in Table 4. Data for the total oxygen content of the stone were calculated from the analysis of the apparently dried inorganic phase as given by Wöhler and Hörne (1859), and on the basis of oxygen in the water and organic extract (Mueller, 1953). The remainder of the data are also from Mueller's paper; the chlorine content of the total stone was not determined.

It is interesting to note that the proportions of the elements in the organic phase of the meteorite are more or less similar to their proportions in the Earth's crust, although the carbonaceous complex of the meteorite is richer in oxygen and seems to have chlorine.

The organic nature of the chlorine in the extracts was demonstrated by failure of a silver chloride precipitate to form on prolonged boiling of the extracts with a silver nitrate solution. These results indicate that the extractable fraction of the carbonaceous phase of the meteorite may contain organic acids containing nitrogen and sulfur groups. Although chlorine may also be part of such a complex, the possibility cannot be overlooked that it originated in the chloroform used for extraction.

No additional organic extracts were obtained following nitration of the residual portion of the meteorite. This observation was interpreted to indicate a low proportion, if any, of aromatic structures or molecules in the non-soluble carbonaceous phase. Insufficient material prevented Mueller from carrying out more detailed chemical examination of the extracts.

Thermal decomposition curves of carbonaceous chondrites are of theoretical interest as they cast light on the possible conditions that prevailed during and subsequent to the final accumulation of the meteorite substance. In this respect, however, care must be taken to consider the variability of water with humidity, temperature, and pressure already noted. Figure 2 shows thermal decomposition curves for the organic extracts from and for the total substance of the Cold Bokevelt meteorite (Mueller, 1953). Also shown are data for the total Orgeuil carbonaceous chondrite (Mueller, unpublished work).

Origin of Carbonaceous Phase in Meteorites

Throughout much of the nineteenth century it was generally believed that complex organic molecules would form only through the agency of living organisms. As a result, it was supposed that the presence of carbonaceous substances within some of the meteorites would be indicative of life on their respective parent bodies. Much later the formation of organic substances in carbonaceous meteorites was explained through hydrolysis of meteoritic carbides with terrestrial water (Spielmann, 1924). This hypothesis is, however, contradicted by the absence of any signs of post-fall reaction rims traversing the chondrites. In spite of the unlikelihood that carbides are the source of the carbonaceous phase, it is evident, from modern chemical experience, that simple groups, which have been spectroscopically detected in stars and other celestial bodies, could condense non-biogenically to mixtures of more or less complex molecules under highly variable physico-chemical conditions.

The main tendencies in the histories of practically all celestial bodies appear to be cooling and condensation; the reverse is restricted to briefer periods of time or to restricted locations, such as the perihelion position of comets or volcanism or metamorphism in planets. This cooling tendency must be kept in mind when attempting to reconstruct those processes that might lead from constituent atoms of the carbonaceous phase to their simple molecules and finally, their organic complexes. It must be stressed, moreover, that, because of the "geological time scale" inherent in the condensation of a celestial body many reactions requiring catalysts in the laboratory may proceed with good yields under less specific conditions. The possible presence of solid particles of diverse composition, and the photochemical effects of radiation, may be particularly favorable factors in promoting the build-up of complex organic molecules in the cosmos.

A very great variety of reactions may contribute to the emergence of organic molecules containing oxygen, nitrogen, sulfur, and possible subordinate quantities of other elements. Considering ranges of physical and chemical conditions, their reactions can be subdivided into 5 more or less arbitrary groups. This classification is based upon increasing specificity in relation to cosmic conditions and, therefore, on corresponding decreasing estimated importance in the universe.

Polymerizations and Condensations in Quasi-Homogeneous Systems at Low Temperature and Pressure

Under these conditions, carbon chains containing one or more double and triple bonds can form, as shown in the following generalized equation where X is hydrogen or any other appropriate organic or inorganic group:

$$CX_2{=}CXH + HXC{=}CX_2 \rightarrow CX_2H{-}CX{=}CX{-}CX_2H$$

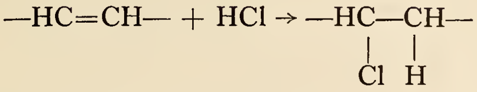
Also possible is the saturation of olefinic or partial saturation of acetylenic bonds through addition of the following elements to the unsaturated carbon atoms: H and CN, Cl and OH, Cl and NO, H and Cl, H and Br, H and I, H and SO_3H, H and OH. Aldehydes and ketones can also react with hydrogen cyanide or ammonia, and numerous other condensations, such as the Wöhler reaction, can occur:

$$NH_3 + HCNO \rightarrow \underset{\text{Urea}}{H_2NCONH_2}$$

Certain molecular structures condense very readily at low temperatures and pressures. Examples of such reactions are the condensations of formaldehyde or acetaldehyde, or the polycondensations of formaldehyde with phenol or urea. These reactions all proceed at pressures below one atmosphere and at temperatures below 200°C.

Reactions involving unsaturated carbon chains could produce long-chain and ring-type molecules. These reactions may be characteristic of those conditions expected to prevail on celestial bodies having radii of 1000 km or less, where the gravitational loss of hydrogen would render the hydrocarbons unsaturated, and where temperature and pressure would be too low for other types of condensations.

Addition reactions, such as that between H and Cl with a double bond



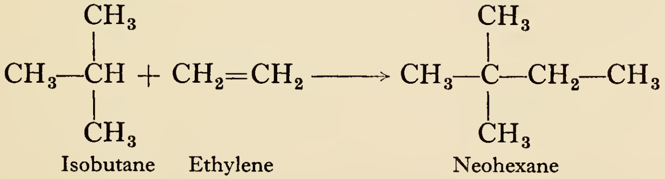
$$\mathrm{-HC{=}CH- + HCl \rightarrow -\underset{\displaystyle Cl}{\underset{|}{HC}}-\underset{\displaystyle H}{\underset{|}{CH}}-}$$

may occur frequently, but they add merely to the complexity of the resultant molecule and do not normally contribute to its chain length.

Polymerization and condensation reactions involving ketones and aldehydes probably did not develop to any appreciable extent under the random statistical conditions governing reactions during the incipient condensation of the celestial body. A possible exception might be in reactions between formaldehyde and nitrogen compounds inasmuch as spectroscopic data for cometary atmospheres has shown them to contain a high proportion of groups such as CN, NH_2, CO, CH, etc. For this reason, the occurrence of carbon–nitrogen polymers in carbonaceous chondrites may be of considerable interest.

Condensations and Polymerizations in Quasi-Homogeneous Systems at Elevated Temperatures and Pressures

Condensations between olefins, or between olefins and paraffins, are possible at elevated temperatures and pressures. Thus, it was found by O'Kelly and Sachanen (1946) that at 500°C and under a pressure of 4500 psi, isobutane is alkylated with ethylene to yield neohexane:



$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{CH}}}} + CH_2{=}CH_2 \longrightarrow CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_2{-}CH_3}$$

Direct coupling of simple gases can also lead to the formation of complex organic molecules. Thus, molecules that seem to be particularly abundant in the cosmos CO and H_2O, can be condensed by several processes. The classic method devised by Fischer and Tropsch (1926) produces higher hydrocarbons and oxygenated products. Condensation requires pressures of 1–5 atm, temperatures between 200° and 300°C, and catalysts such as cobalt, iron, thorium, or silicon compounds, all of which are rather likely to occur, at least in traces, in various cosmic settings. The polymerization of HCN has also been studied (Werner and Grey, 1947), and it has also been shown that CO, H_2S and other simple molecules can add to olefins.

From these few examples, involving molecules with relatively higher H/C and O/C ratios and increased temperature and pressure, it appears that such reactions are more likely in the case of celestial bodies with dimensions of approximately those of the Earth. The resulting complex molecules are expected to be more saturated than those produced at lower temperatures and pressures. The high hydrogen saturation of celestial bodies much larger than Earth may tend to prevent the formation of large organic molecules through hydrogenation and cracking.

Reversible condensations—Condensations of easily reversible character proceed only with good yields when a simple molecule, usually water, is eliminated from the system. Ethers, esters, and anhydrides are formed through the following general equation where X is any group except OH or O, and Y_2 is H_2, O, or any group except OH:

$$XY_2COH + HOCY_2X \rightleftharpoons XY_2C—O—CY_2X + H_2O$$

The presence of molecules with oxygen bridges in a carbonaceous complex may indicate that they formed under conditions where the water eliminated could escape, assuming that temperature and pressure conditions would permit such escape.

Reactions between molecules that can form only under differing conditions—Nitration, the formation of peroxides, or the formation of diazo compounds that can subsequently couple, occurs between molecules differing greatly in their oxidation states. The oxidation of methane under controlled conditions may yield methyl alcohol, but in other instances dehydration followed by condensation may also result. Thus, oxidation of benzene may yield biphenyl:

$$\underset{\text{Benzene}}{2C_6H_6} + (O) \rightarrow \underset{\text{Biphenyl}}{C_6H_5—C_6H_5} + H_2O$$

Similar processes may cause the polymerization of petroleum to asphalt in surface zones of terrestrial deposits, and a similar process was reported for the oxidative polymerization of coals (Karavaev, 1953).

The presence of organic molecules formed through interaction of substances of various oxidation states may be indicative of a surface reaction. Only at such a location can the molecules from radically different settings, such as the solid phase and the atmosphere or hydrosphere, interact. Unfortunately, there are no diagnostic criteria available for recognition of such reactions. Stability over geological time of nitro, peroxi, or similar groups is doubtful, and the resultant products from oxidative dehydrogenation of molecules cannot be distinguished from those forming from the union of unsaturated chains.

Reactions unlikely to occur under any conceivable cosmic conditions—Certain reactions used for the synthesis of organic molecules in the laboratory are unlikely to occur to any appreciable extent in nature.

Thus, for example, reactions of the Grignard type could not be expected because the presence of free magnesium would be prevented in the cosmos by the high abundance of oxygen.

From the above considerations it can be concluded that those molecules most likely to build up organic complexes in the cosmos are unsaturated or oxygenated. Saturated hydrocarbons are not known to condense under normal laboratory conditions, and are unlikely to condense at higher pressures inasmuch as the reaction would involve liberation of hydrogen. It appears, therefore, that organic complexes of non-biogenic origin can only be expected in systems having high C/H and O/H ratios and at temperatures below about 800°C. Of the celestial bodies, only the carbon stars seem to contain the necessary favorable ratios, possibly because of the elimination of the bulk of their hydrogen in the operation of the carbon cycle. Thus, a carbonaceous phase might be expected within such bodies containing anomalously low hydrogen content once their temperatures dropped sufficiently. All cooler condensations of matter or of near mean cosmic composition, and down to the dimensions of the major planets, would be expected to contain little or no complex organic phase. Only with decreasing size of the parent body, as already explained, would appearance of a carbonaceous phase be anticipated.

The proportionality of types of organic molecules constituting the carbonaceous phase would perhaps primarily depend upon the original elemental composition of the atmosphere of the parental body. This is not to say, of course, that pressure, temperature, radiation, and other factors do not also play vital roles. The original elemental composition of the atmosphere, moreover, would mainly depend upon the size of the celestial body, and it should be noted again that in an intense gravitational field relatively more paraffinic structures would form because of the higher abundance of hydrogen. On smaller bodies, the organic products would be more highly oxygenated and carbonized. Extrapolating further, it is possible that on very small bodies, particularly if they had been at high temperatures, there may be left only residual carbon. Thus, a celestial body of "optimum" size is possible, perhaps one with dimensions between those of the Earth and the Asteroids, in which high-molecular-weight organic substances would reach maximum concentrations.

Many workers have in very recent years considered the possibility of extraterrestrial life from diverse approaches; conclusions reached have not always been the same. Thus, Abelson (1961), taking into consideration factors such as water and temperature, concluded it to be unlikely that terrestrial-like life exists on the Moon, Venus, or Mars. Moreover, it was also concluded that it would be virtually impossible to contaminate these bodies with rocket-carried implants from Earth, for life as we know it could not exist on these bodies. In contradiction to this conclusion, it has been noted that simpler, early organisms might still survive and thrive on Mars. As further pointed out by Lederberg (1960), many students of Mars are of the opinion that that planet already has its own biota. Obviously, there are fundamental differences of opinion on the matter of extraterrestrial life. In view of such differences, and until more specific evidence one way or the other can be obtained, the existence of such life cannot be disregarded.

The origin of life processes, basing the analogy on terrestrial experiences, is dependent upon the formation of proteins, carbohydrates, liquids, and those molecules with memory characteristics which establish a pattern of specialized structure where otherwise randomness would prevail. Although but little is known as to the origin of such molecular structures, it is known that irradiation of mixtures of methane, ammonia, water, carbon dioxide, and other gases with high energy radiations, ultraviolet light, or electrical discharge will lead to the formation of amino acids, the building blocks of proteins (Miller and Urey, 1959). Similarly, it is possible that more complex structures, such as the purines or pyrimidines that are precursors of nucleic acids, could also be formed (Calvin, 1960). Using such techniques as ultraviolet, infrared, and mass spectroscopy, along with chromatography, Calvin and Vaughn (1960) recently found evidence for heterocyclic aromatic bases and, possibly, for reducing sugars in both the Murray and Orgeuil carbonaceous chrondrites. The occurrence of such biologically significant substances points to the possible existence of biological systems on bodies other than Earth.

Recently a detailed study of the Orgeuil carbonaceous chrondrite has been carried out in a continuing effort to obtain data on the origin of the organic matter (Nagy, Meinschein, and Hennessy, 1961). Using primarily distillates and mass spectroscopic techniques, and comparing the mass spectra to those for hydrocarbons from butter and recent sediments, these authors reported that the composition of the hydrocarbons obtained from the meteorite warranted the conclusion that they may have been derived through biological processes.

It should be pointed out that the conclusions based upon study of a sample, such as the Murray or Orgeuil carbonaceous chrondrite can be no better than the sample itself. In this respect it is particularly important to note that most museum specimens available for chemical study have been shellacked, waxed, coated, written upon, or otherwise handled under the worst possible conditions (Henderson, E.P., personal communication). In view of the broad range of contaminants, both as to type and quantity, it is essential that such factors be considered in arriving at any conclusions on the basis of analytical data.

On examination of the Orgeuil meteorite, Claus and Nagy (1961) reported evidence for biological activity in the form of unusual organized structures, unknown on Earth, and thought to represent extraterrestrial organisms. If these organized elements actually are, as concluded by Claus and Nagy, microfossils indigenous to the meteorite, then a great step has been taken forward in demonstrating the occurrence of extraterrestrial life and the biogenic origin of the organic phase of carbonaceous chondrites.

Carbonaceous Phases as Cosmological Indicators

Once the carbonaceous phase is finally formed in a meteorite, the highest temperature in its history tends to be "frozen in". In this way the organic phases may serve as useful indicators of the physical and chemical conditions that prevailed in the extraterrestrial setting. With this in mind, and considering also the "C—H, O, N, S equilibrium", it is possible to reconstruct the following histories for the parent bodies of various types of meteorites in broad outline.

The siderites contain carbon mainly in the form of graphite, and liberate hydrogen upon heating. Such data can be taken to indicate that the carbon and hydrogen were essentially dissociated during the highest temperature phase of the meteorite, and that the temperature was most likely over 2000°C. The rarity of diamonds (Nininger, 1939) seems to indicate that pressures were not particularly high.

The chondrites contain essentially amorphous carbon and liberate primarily CO_2 on heating. This equilibrium indicates a lower maximum temperature for the history of the meteorite. In analogy with Earth, the siderites can be considered to be part of the core of a parent body, whereas the chondrites, with or without dispersed iron phase, may have originated in the mantle where temperatures were never as high as those in the iron–nickel core.

The intense decomposition of the hydrated silicates and the organic material of the Cold Bokevelt and Orgeuil meteorites below 200°C demonstrates that these stones could not have been heated above that temperature. In view of the low thermal conductivity of silicates and the fact that frictional heating effects are of short duration, there are strong arguments that the interior portions of the stones were not heated above this temperature during fall. The presence of fused surface crusts only a few tenths of a millimeter in thickness shows that only the external surfaces of the stones were heated to temperatures of 1000°–1200°C necessary for their fusion.

Assuming an inorganic origin, these considerations can be used to account for a possible mechanism for the inclusion of carbonaceous matter in the meteorites. Thus, it is possible that the condensing body, with metallic and silicate particles only roughly segregated in a rather low gravitational field, would release appreciable quantities of occluded gases as temperature increased in the deeper zones with progressive condensation. These gases would partially condense on the cooler surface, and some of the products would be swept to the tail-end of the body by the fine particles still falling towards its surface. Possible weak volcanic activity or impacts of larger meteorites could mix the material in the close-to-surface zones. This last factor could explain the chondrules and occasional fused rock fragments in the carbonaceous stones; the chondrules are thought by the author to indicate fusion of rock in a low gravitational field in which a system of globules of liquid in gas, the opposite of terrestrial vesiclar rocks, may survive long enough for the solidification of the fused silicates.

The variable composition of the inorganic phase of carbonaceous meteorites, when compared to other chondrites, further indicates close-to-surface conditions; as already noted, organic oxygen bridges may also point towards the same conditions.

The achondrites, particularly those highest in SiO_2 and Al_2O_3 and of "basaltic" composition, represent a lighter fraction of the silicate melt. If the conclusions drawn from the carbonaceous meteorites are, however, correct and they represent a surface zone, then the achondrites cannot be derived from a still higher zone of the same parent body. Therefore, a separate parent body has to be postulated for the acondrites, one of relatively larger size with a higher maximum temperature to cause fusion of the silicates, and a more intense gravitational field to account for the separation of a surface zone of lower density.

These hypotheses lead to the conclusion that the carbonaceous chondrite and the achondrites of basaltic composition originate from two different types of parent bodies. The "dual origin" theory does not, however, eliminate the possibility that both classes of celestial bodies may fragment to yield siderites, stony-irons, chondrites, or achondrites.

As has been noted, the mean H/C ratio of the carbonaceous complex would be expected to rise with increasing size of the parent body. On the other hand, the surface of a relatively large body would tend to be more sialic in composition as has just been noted.

The apparently very high sulfur content of the organic phase of the meteorites may be related to the anomalously low concentration of the element in the inorganic phase. It is conceivable that, because of the smaller gravitational field of the parent body of the meteorite, a higher than normal proportion of sulfur would migrate into its atmosphere than is the case on Earth.

It may be considered possible that there is a similarity in the composition of carbonaceous complexes from different celestial bodies. Even assuming a biogenic origin for the substances, it may be difficult to differentiate the initial effects of life processes from later changes imposed on the initial material by physical and chemical conditions. Such effects would also tend to destroy recognizable remains of higher organisms (see Claus and Nagy, 1961). The following criteria could, however, be used in an attempt to determine the source of the carbonaceous matter of chondrites:

(1) C^{12}/C^{13} and S^{32}/S^{36} ratios. Scanty data for the carbon ratios indicate a non-biogenic origin for the carbonaceous complexes.

(2) Organic structures of biogenic origin. The occurrence of compounds related to chlorophyll or of carotenoids would be extremely significant. The work by Calvin and Vaughn (1960) already noted, in which indications have been found for structures related to pyrimidines or purines, is most encouraging.

(3) Optical rotation. The detection of optically active compounds in carbonaceous meteorites would, based upon terrestrial experience, unquestionably point to a biogenic origin for the material. The absence of

such activity in the extracts from the Cold Bokevelt meteorite indicates, but does not prove, a non-biogenic origin.

(4) Trace elements. The distribution of minor elements between the organic and inorganic phases of a meteorite may throw light upon the origin of the carbonaceous material.

Although there is considerable evidence that organic substances in meteorites may be of a non-biogenic origin, a biogenic source for the material cannot be disregarded. As has been noted, the organic material could have originated in zones close to the surface of a parent body under conditions which, at least during certain periods of time, may well have been within the range under which primitive organisms could have evolved and propagated. There is no reason why such organisms could not adapt themselves to non-terrestrial conditions.

The hypotheses presented in this chapter represent an attempt to explain extraterrestrial carbonaceous material on the basis of the best, if scant, pertinent information available. With exploration of outer space by man very near at hand, much critical data will undoubtedly become available for use in re-evaluating and testing the tentative and hypothetical suggestions that have been made.

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CHAPTER 2

PREBIOLOGICAL FORMATION OF BIOCHEMICAL SUBSTANCES*

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Introduction

MANY kinds of thought have been brought to bear on the geochemical nature of the prebiological world. Since only 1950 (Garrison, Morrison, Hamilton, Benson and Calvin, 1951), serious experimentation by investigators who were leaders in other areas of science has begun. This kind of activity was not at first generally regarded as respectable, nor as likely to lead to meaningful results within our lifetimes. The acceleration of experimental activity in this field, however, symbolizes a rapidly changing outlook. The belief is growing that theories derived from inferences of the nature of the prebiological world can be tested against knowledge of the chemical composition and behavior of organisms. The subtle interplay between experiment and theory in this field may be expected to provide a means of checking our various inferences about organic geochemistry before life appeared and before life altered it in some as yet undetermined degree.

From a geochemical point of view, perhaps the weakest point in this kind of experimental discipline is that life theoretically could begin from a very special set of conditions obtaining in one locale only, and that these conditions and identity and balance of compounds did not necessarily apply throughout much of the terrestrial continuum. The knowledge of the unity of biochemistry (Kluyver and Van Neil, 1956), however, suggests that the nutrients of the first organism had essentially to be on hand for the nurture of the offspring of that first organism. On this basis it seems likely, albeit unnecessary, that the chemistry of the first organism reflected closely the average geochemical matrix, rather than that of a special island of material.

From the point of view of biology rather than that of geochemistry, the problem can be seen to derive its structure from many fields of science: geology; biology; organic, inorganic, and biological chemistry; as well as astronomy. It seems clear, however, that the branch of chemistry most involved is that of organic (or bio-organic) chemistry, and the nonchemical science most involved is that of geology. It is accordingly appropriate to treat this topic under the heading of organic geochemistry, and there can be much hope that a correct solution will serve as a platform from which to climb to new knowledge in geochemistry. As in organic chemistry, a complete experimental synthesis is most likely to be regarded as certification of a correct analysis of the structure. When a living cell is first synthesized, however, the question can then be asked not only as to what extent the supporting conditions represented the primitive earth as a whole, but to what degree this life resembles original life.

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* Submitted in 1958.

Most of the concepts of the prebiological world since 1950 and virtually all of these concepts before 1950 have a dialectical basis rather than an experimental foundation. The emphasis in this presentation will be thrown, however, to the experimental foundation and some of the disputations will be arranged around those. Experiments are, in a sense, no more disciplinary than observation in view of the need for interpretation in either case, but experiment often reveals phenomenological facets which man's mind was practically incapable of visualizing in advance.

The carbon compounds which can be visualized as prebiological could arise in the primitive atmosphere, hydrosphere, or lithosphere. Suggestions for each of these will be discussed in their appropriate locales.

Simple carbon compounds on the primitive earth—The division of the earth into lithosphere, hydrosphere, and atmosphere is an artificial one to the extent that it leads to thinking of these realms discontinuously. Their separation is possible on the basis that solids, liquids, and gases are interconvertible only through appropriate physical transition states. Chemically and physically they are highly continuous, perhaps especially so in a primitive condition at more elevated temperatures.

In the lithosphere the source of carbon compounds that has received attention is that resulting from metallic carbides. This notion has been treated in detail by Oparin (1957) who also emphasizes the hydrocarbons. Inasmuch as the significance of the hydrocarbons in petroleum is treated elsewhere in this volume, this aspect will not be considered in this chapter.

Inorganic carbides can function as a doorway to organic compounds through reaction with water to form acetylene. The well known reaction of calcium carbide proceeds:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + HC{\equiv}CH$$

The course of the reaction with the carbide of iron, Fe_3C (cementite) is somewhat different and more complex, and is known to yield methane, ethane, ethylene, and other hydrocarbons (Oparin, 1957).

The conversions of acetylene to acetaldehyde and to acetic acid are rudimentary reactions of modern organic chemistry and can be imagined to lead to a host of carbon compounds. An experimental program in this context deserves more attention than it has yet received.

The possibilities in the primitive atmosphere have received the most attention of the three realms. The simple one-carbon compounds which have come into purview are carbon monoxide, carbon dioxide, methane, formaldehyde, and formic acid. Other one-carbon compounds such as urea, carbamyl phosphate, and hydrocyanic acid can be considered under strict interpretation of this category, but only those containing carbon, hydrogen, or oxygen will be treated for the sake of feasibility. For similar reasons, free radicals such as $\cdot CH_2 \cdot$ will not be considered here.

The inferences on carbon dioxide in the primitive atmosphere range from virtually none to 91% by volume. The latter figure is from a tabulation by Rubey (1955) (Table 1).

TABLE 1

Rubey's Proposed Early Atmosphere and Ocean (1955)

Component	Atmosphere Percent by Volume	Solute in Ocean 10^{20} g
CO_2	91	240
N_2	6.4	0.2
H_2S	2.0	12
HCl	0.2	310
H_2O vapor	0.2	
NH_3	0.01	14
H_3BO_3		7.4
HBr		1.0
HF		0.3
CH_4	0.02	0.004
Cl_2	0.01	0.2
CO	1 ppm	1 ppm
H_2	1 ppm	1 ppm

Rubey arrived at his figures by considerations of equilibrium reactions in which compounds of the critical elements are present. "The basic assumption is that the 'excess' volatiles (that is, those materials present in today's atmosphere, hydrosphere, and biosphere and entombed in ancient sediments that cannot be accounted for by rock weathering) afford the best . . . direct evidence of the probable composition of the early atmosphere . . ." The assumption that these volatiles are truly juvenile is a large one, as it ignores the possibility of changes wrought by organisms.

Formation of Formaldehyde and Formic Acid

In the present experimental era, the first of the papers describing experiments devised to provide understanding of the terrestrial origin of organic compounds of biological significance is found in the work of Garrison and associates (1951). These workers bombarded air-free aqueous solutions of C^{14}-labeled carbon dioxide in a closed system with and without the addition of ferrous sulfate. The bombarding beam was one of helium ions, and products identified were formaldehyde and formic acid. In one experiment, one-fourth of the carbon dioxide was reduced by water by this treatment.

These results have been discounted by Urey (1952) who claimed that Oparin's arguments were ignored by Garrison and co-workers. It is not necessarily true that these arguments were ignored, but perhaps that the Berkeley workers were not prepared to accept unquestioningly the thesis of an initial set of anaerobic conditions. Urey also makes the point, however, that difficulty is encountered in accounting for the origin of organic compounds from inorganic compounds. In this paper Urey presents some of the arguments for and against the occurrence of oxygen and carbon dioxide in the original atmosphere, relying heavily on a treatment of equilibrium constants.

Urey points out, for example, that the equilibrium constant, K_{298} for

$$C + 2H_2 \rightleftharpoons CH_4$$

is 7.8×10^8. If hydrogen were present, then CH_4 must also have been present.

Oparin's arguments for the presence of hydrogen have been advanced in the third edition of his book on *The Origin of Life*. This picture has been formed in part from his tracing of the metamorphoses of the simple compounds that he considers. He argues that the oxygen which was continuously produced, by photolysis of water vapor in the upper atmosphere, must have been consumed by reaction with other substances. Oparin also points to the calculations of Rabinowitch (1955) which show that the entire amount of free oxygen in the atmosphere could be produced by vegetation in only 2,000 years. He also states that only the outermost skin of the earth is oxidized; deeper formations such as black, green, or grey lava or basalt can be seen, by virtue of their colors, to contain iron in an incompletely oxidized state.

Oparin objects to the inclusion of carbon dioxide in the primitive atmosphere on the basis that this would be an already highly oxidized compound which would then have to be converted to organic compounds of high energy. Calvin and co-workers have shown how this could have occurred although their work does not answer the objection of prior oxidation of carbon to carbon dioxide. The concept of primordial carbon dioxide violates a premise, however, rather than an experimental verification of an hypothesis. On the positive side, Oparin points out that Miller's experiments (see below) with the Oparin-Urey type of atmosphere resulted in the synthesis of amino acids. This presumed vindication lost some of its force when many other workers were also able to produce amino acids under other sets of conditions which could also be inferred as prebiological (see below also).

Oparin also recognizes the argument that carbon dioxide is a "juvenile" gas (Poole, 1951; Goldschmidt, 1952). The rebuttal to this lies in the explanation of Vernadskii that carbon dioxide in the gases from volcanoes is merely that which results from decomposition of preformed carbonate (Oparin, 1957).

Rubey, however, concluded that "carbon dioxide has been supplied by the atmosphere and ocean gradually and at about the same rate that it has been subtracted by sedimentation" and noted that the reasoning for this conclusion has been ignored even though repeatedly expressed (Rubey, 1951).

It should thus be clear, from citation of some of the main arguments pro and con, that the presence or absence of primeval carbon dioxide is a question that evokes two or more current answers. It is not surprising that with this background the interpretations of such experiments as Garrison's are also controversial. It seems to this author, at least, that if one considers the production of amino acids from methane, hydrogen, water and ammonia by electrical discharge as evidence for a carbon dioxide-free prebiological atmosphere, he must also consider Garrison's experiments seriously as evidence for a carbon dioxide-rich atmosphere.

Formation of amino acids—Few or no experimental investigations have aroused as much lay and scientific interest in natural concepts of the origin of life as the first report of the production of amino acids by electrical discharge in a mixture of ammonia, hydrogen, methane, and water (Miller, 1953). The interest in this advance undoubtedly stems from the fact that the amino acids are constituents of the proteins, which are so essential to life (Fox and Foster, 1957).

As one looks back from the perspective of 1960, one can see many comparable instances of production of amino acids. These are perhaps best treated chronologically, in which case the work of Löb (1913) first becomes of interest.

The objectives of Löb appear to have been those of simulating chemically the biological fixation of nitrogen, rather than of understanding primordial chemistry. The reaction mixture used represents, however, material which has significance in the context of prebiology, due particularly to the recent emphasis by Revelle (1955) on carbon monoxide in the primitive atmosphere.

Löb obtained a small quantity of glycine when he subjected a moist mixture of carbon monoxide and ammonia to silent electric discharge and presented experimentally derived reasons for believing that the reactant gases yielded formamide, $HCONH_2$, as an intermediate. Although the quantities obtained by Löb would be ample for assignment of structure in the modern era, he found it necessary to prepare the naphthalenesulfonyl derivative and to confirm the identity of glycine by the melting point of this derivative and its mixed melting point with authentic naphthalenesulfonylglycine.

For his first experiments, Miller (1953) reported the production of aspartic acid, glycine, α-alanine, β-alanine, and α-amino-n-butyric acid from a mixture of methane, hydrogen, water and ammonia. Products were identified by two-dimensional paper chromatography. In Miller's first long paper (1955), the separation of amino acids on Dowex-50 and silica columns was described. Compounds recorded were glycine, α-alanine, β-alanine, sarcosine, α-amino-n-butyric acid, α-aminoisobutyric acid, unidentified amino acids and glycolic, lactic, formic, acetic, and propionic acids.

Abelson (1956) confirmed Miller's production of amino acids and also succeeded in obtaining them by electrical discharge in such mixtures of gases as CO_2—H_2—H_2O—N_2, CO—H_2—H_2O—N_2, and CO_2—H_2—H_2O—NH_3. It is obvious that the presence of carbon dioxide permits the production both of amino acids and of organic acids *à la* Garrison; the presence of methane is not necessary to produce amino acids in this way. It should be pointed out, in addition, that carbon dioxide was identified in Miller's products and must, therefore, have been produced in some stage in the sparking.

TABLE 2

*Mixtures of Gases Yielding Ninhydrin-positive Reactions on Electrical Discharge**

	Composition of Gas Volume per cent						Ninhydrin-positive reaction
Expt.	CH_4	CO_2	NH_3	N_2	H_2	O_2	
1	40	—	40	—	20	—	+
2	40	—	40	16	—	4	+
3	6.7	53.3	26.7	13.3	—	—	+
4	—	50	—	50	—	—	—
5	—	50	50	—	—	—	+

* Heyns, Walter, and Meyer, 1957

Heyns, Walter, and Meyer (1957) obtained positive ninhydrin reactions for the products of electrical discharge in a number of mixtures of gases (Table 2). Of much interest is experiment no. 5 in which only CO_2 and NH_3 were present. No amino acids were identified, but amines are a possibility. The ninhydrin test is positive for amines as well as for amino acids, the significance of the formation of amines under these conditions being less than for amino acids. The finding of ninhydrin-positive products in the presence of oxygen (experiment no. 2) is also provocative, but the results are open to the same question.

Pavlovskaya and Passynskii (1959) tested electrical discharge in a gaseous mixture which was the same as that originally proposed by Urey and Oparin except that hydrogen was replaced by carbon monoxide. The mixture was, therefore, CH_4—CO—H_2O—NH_3. Electrical discharge yielded glycine, α- and β-alanine, α-amino-n-butyric acid, aspartic acid, and glutamic acid.

Bahadur (1954) reported the synthesis of amino acids by exposure of an aqueous solution of paraformaldehyde, potassium nitrate, and a small amount of ferric chloride to bright sunlight for 80 hr. Many amino acids were obtained and their identities were dependent upon the proportions of reactants. In one case the following were identified chromatographically: valine, histidine, proline, lysine, serine, aspartic acid, glycine, asparagine, and arginine. More certain identification was documented for serine, aspartic acid, and asparagine. Serine was recognized by its conversion to two other compounds. Aspartic acid and asparagine were recognized by the melting points of their derivatives.

In a later paper, Bahadur (1958) reported the startling discovery that nitrogen of the air could replace the nitrate if colloidal molybdenum oxide were present as the catalyst; an ordinary 500W artificial electric light bulb was used.

Pavlovskaya and Passynskii (1959) reported results similar to those of Bahadur. When ammonium nitrate was used, the spots identified by paper chromatography corresponded to valine, alanine, glutamic acid, and glycine. With ammonium chloride instead of the nitrate, chromatography suggested, in addition, basic amino acids.

Although their work was not directly related to study of the origin of life, Hasselstrom, Henry, and Murr (1957) produced glycine, aspartic acid, and diaminosuccinic acid by exposing an aqueous solution of ammonium acetate to beta radiation.

Paschke, Chang, and Young (1957) reported the production of glycine and possibly alanine by gamma irradiation of ammonium carbonate. These authors emphasized the fact that they used as starting material a completely oxidized form of carbon in the absence of hydrogen. Glycine was identified by paper chromatography in each of five solvent systems. The presence of alanine, also suggested, was not fully confirmed.

Dose and Rajewsky (1957) subjected mixtures of gases comprising CH_4, CH_2, H_2, H_2O, N_2, and NH_3 to X-rays. The products were separated on electrophoretograms and were identified generically by reaction with ninhydrin. Many individual products, classified by the authors into groups as acid amino acids and amines, were identified. The latter could have been basic amino acids entirely or in part.

Amino acids can be produced by heating ammonia or urea with hydroxyacids such as those that function as biological intermediates, e.g., malic acid or fumaric acid. Most notably, aspartic acid (Fox, Johnson, and Middlebrook, 1955) can be formed in this way. In unpublished work, Harada, Johnson and Fox have found that α-hydroxyglutaric acid is converted in a similar way to glutamic acid. In other unpublished work, up to seven ninhydrin-reactive spots were obtained chromatographically from the reaction of only one or two amino acids. Also, the heating of glucose and urea gave a spot identified as that of glycine in three solvent systems. Additional studies have been published by Fox, Johnson, and Vegotsky (1956); Fox (1956); Fox, Vegotsky, Harada, and Hoagland (1957); Fox (1957); and Fox (1958).

Heyns and Pavel (1957) have found that heating glycine with quartz sand at 260–280° yields alanine and aspartic acid. In addition, they presented evidence that gases formed by decomposition of amino acids can be recombined to re-form amino acids.

To summarize, although not all reports of the production of amino acids under presumably primitive conditions have been adequately verified, there can be little doubt that the majority of them are correct. What is more significant is that there can be little doubt that numerous mixtures of simple compounds, under the influence of various sources of energy, yield one or more amino acids. The production in one or more of these contexts of some of the amino acids not yet described, such as phenylalanine, leucine, tryptophan, and methionine will be awaited with interest. The amino acids are thermodynamically relatively stable (see Oparin, 1957, p. 154) and it was expected by some, and is now established, that experiments with simple compounds cast in the geologically prebiological mode are more likely than not to yield amino acids. A corollary of this is the inference that amino acids and the much more complex system of chemistry known as life is an inevitable consequence of matter which anywhere undergoes the evolutionary process which has occurred on this planet.

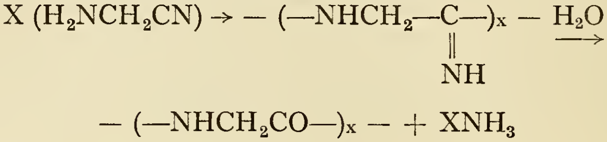
Formation of protein—At present the possibilities for primordial production of protein appear to be more limited than for amino acids. In considering the primordial synthesis of protein, one has among other choices one of two working hypotheses.

One of these hypotheses visualizes the first polymeric protein-like substances on the earth as simple structures (Akabori, 1958; Bernal, 1958). Akabori invoked what he calls "fore-protein", which is at the outset simple polyglycine. Bernal argues as follows, "It is conceivable, though I think unlikely, that no such stage of solution of monomers or oligomers such as amino acids, simple peptides, or sugar molecules ever existed and the formation of such molecules went *pari passu* with their polymerization." In this quotation, Bernal has coupled what is probably an entirely defensible statement with one that he admits to be open to question. An alternative, but not exactly opposite, point of view is that the simple compounds existed but functioned also essentially as transitory intermediates in polymerizations. The arguments for the point of view of rapid simultaneous reactions are that this is the only way we know that any living cell functions, and that the striking biochemical similarity of all organisms studied (Kluyver and Van Niel, 1956) is most consistent with a similar prebiological chemistry (Fox, 1957). Akabori and co-workers have provided a model for the simple fore-protein and Fox and co-workers have provided a model for a primordial protein of complexity comparable to that of current protein.

The two modes mentioned are the two principal mechanisms which have appeared. The possibility of polymerization of amino acids through electrical discharge might seem to be ruled out by the failure of Miller (1955) to find biuret-positive reaction products in his materials. Otozai and collaborators (1954) claim, however, to have produced "some sort of polymer of glycine" by electrical discharge in glycine. This report was very inconclusive because the material was inadequately characterized.

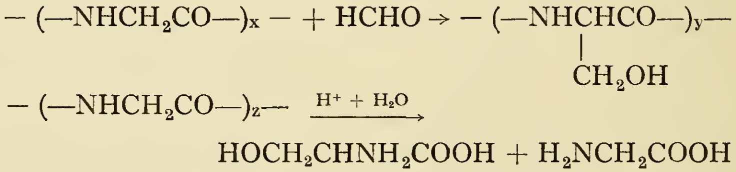
The work of Akabori and colleagues (Akabori, Okawa, and Sato, 1956; Akabori, 1958) begins with polyglycine which is hypothesized to form as follows:

$$HCHO + NH_3 + HCN \rightarrow H_2NCH_2CN + H_2O$$



$$X\,(H_2NCH_2CN) \rightarrow -(\text{—}NHCH_2\text{—}\underset{\underset{NH}{\|}}{C}\text{—})_x- \xrightarrow{-\,H_2O} -(\text{—}NHCH_2CO\text{—})_x- + XNH_3$$

For the experimental work, polyglycine was made by another, conventional, chemical process and was dispersed on kaolinite. This material was reacted with formaldehyde and with acetaldehyde. The aldehydes each condensed with the α-carbon atoms of the polyglycine to give, respectively, serine and threonine residues, the amino acids being recovered after hydrolysis:



$$-(\text{—}NHCH_2CO\text{—})_x- + HCHO \rightarrow -(\text{—}NH\underset{\underset{CH_2OH}{|}}{CH}CO\text{—})_y\text{—}-(\text{—}NHCH_2CO\text{—})_z\text{—} \xrightarrow{H^+ + H_2O} HOCH_2CHNH_2COOH + H_2NCH_2COOH$$

The polyglycine was also substituted by reaction with butene-2 at a temperature of 130° and in a second experiment in the presence of a small amount of ozonide, which proved to be necessary. In the former case Japanese acid clay was employed in place of kaolinite. Akabori suggested that the need for ozonide indicated an initial contribution from solar radiation.

Akabori indicated that his hypothesis could explain the chemical evolution of protein molecules from polyglycine to more complicated proteins by gradual introduction of side chains.

By invoking a moderately elevated temperature, it was possible to visualize how amino acids might spontaneously condense to yield protein-like materials. The type reaction in the formation of the peptide bond (here illustrated for a dipeptide):

$$H_2NCHRCOOH + H_2NCHR'COOH = H_2NCHRCONHCHR'COOH + H_2O$$

is one for which the equilibrium is far on the side of hydrolysis. Some means for overcoming the energy barrier is necessary in order for the reaction to proceed in the synthetic direction. One such means that can be visualized is the elevation of temperature above the boiling point of water at the prevailing pressure. As water is thus removed by volatilization, the mass action law requires that the reaction proceed in the direction of synthesis. The geological conditions visualized are those of a hypohydrous magma of amino acids or precursors at a temperature above the boiling point of water. Such temperatures are within the range of Urey's "cold earth" (Urey, 1952) and are of course common in peri-volcanic regions on the earth today.

Much chemical information has been accumulated on the thermal production of peptides by heating amino acids under selected conditions (Harada and Fox, 1958; Vegotsky, Harada, and Fox, 1958). Of most interest in the present context is the finding that operation in this same set of conditions can produce a polymer containing all the common amino acids. Qualitative chromatograms of the hydrolyzates of such materials, designated as *proteinoids*, appear much like chromatograms of casein hydrolyzates (Fox and Harada, 1960).

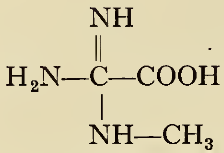
A salient feature of some of the products is that they are not structured in a fully random manner. For example, in one sequence of products (Harada and Fox, 1960) from the copolymerization of glutamic acid and aspartic acid, the glutamic acid content varied between 15% and 29%, but the proportion of glutamic acid in the N-terminal position varied between 54% and 59%; the proportion of glutamic acid at one end of the peptide chains was thus two to three and one-half times as great as in the total mass of peptide. The possibility of visualizing a step by which randomness is modulated to a degree of nonrandomness is believed to be critical in understanding the emergence of life from inanimate matter. The randomness of inanimate matter which is assumed is, however, open to question, at least on the basis of recently recognized non-parity of physical particles (Rodberg and Weisskopf, 1957). It is of interest, in any event, to be able to find in molecular ecology of substances as simple as amino acids, influences which provide the clearly discernible beginnings of a specificity which in its exponentialization is comparable to that which obtains at the biological level, and which is absent at the micromolecular level.

The temperatures recorded are usually in the range of 160–180°. It is known, however, that the addition of phosphoric acid lowers the threshold temperature by 20° to 30°, and it is probable that other undiscovered reactants with catalytic activity will lower the temperature further.

Additional pertinent references regarding the thermal synthesis of protein are: Fox and Middlebrook (1954); Fox, Johnson, and Middlebrook (1955); Fox (1956); Fox, Johnson, and Vegotsky (1956); Fox (1957); Fox, Vegotsky, Harada, and Hoagland (1957); and Fox (1958).

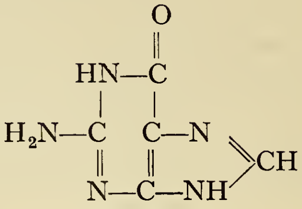
Formation of nucleic acids—Heyns, Walter, and Meyer (1957) were struck by the appearance of guanidinoacetic acid in their experiments at

200°, especially because of the structural resemblance of this compound to the pyrimidines of nucleic acid.



$$\mathrm{H_2N{-}\underset{\underset{NH{-}CH_3}{|}}{\overset{\overset{NH}{\|}}{C}}{-}COOH}$$

Guanidinoacetic acid



Guanine

Ureidosuccinic acid has been obtained as a principal product from the thermal experiments with urea and malic acid (Fox, Johnson, and Vegotsky, 1956). This development was of particular interest inasmuch as this compound has in recent years been documented as a biological intermediate in the synthesis of pyrimidines (Reichard, 1954, and bibliography).

$$NH_3 + CO_2 + \text{L-aspartic acid} \rightarrow \text{L-ureidosuccinic acid} \rightarrow \text{orotic acid} \rightarrow \text{pyrimidines.}$$

Summary

Most of the principal reactions known for the production of biochemically necessary substances under geologically admissible prebiological conditions have been reviewed in this section. The various possibilities are summarized in the following picture:

CO, CO_2, and/or CH_4
NH_3 or N_2
H_2O
H_2
H_2S
Metal atoms
H_3PO_4

$$\xrightarrow[\text{Electricity, Heat, Solar radiation, }\beta\text{-rays, }\gamma\text{-rays, X-rays}]{(1)}$$

Biochemical Staples
(Organic acids, amino acids, vitamins, carbohydrates, pyrimidines, porphyrins, etc.)

$$\xrightarrow[\text{Heat}]{(2)}$$

Macromolecules
Proteins
Nucleic acids
Polysaccharides

$$\xrightarrow{(3)} \text{Organisms}$$

The possible geological settings for the three steps depicted vary according to the step and to the type of physical agent one chooses to invoke. If we continue to restrict our considerations to conditions that are shown to be experimentally consistent, we may further discipline our thinking. In so doing, however, we must recognize that not all of the conceivable experiments have been performed.

Each stage of a picture of what happened perhaps two billion years ago is subject to question. The picture presented represents, however, most of the scope of thinking.

In the first step, the general geological picture is one of the beginnings of formation of organic compounds by interaction of the "excess volatiles" (Rubey, 1955). A favorite mode of thinking is to picture this as occurring in the extralithospheric atmosphere, but a case can be made for the occurrence of such reactions in atmospheric pockets in the interior of the earth rather than in the atmosphere accumulated by outgassing. If these reactions should occur beneath the surface of the earth, the forms of energy which are most consistent are heat and radiation. Above the surface of the earth, any and all of the forms of energy mentioned might operate. The necessary concentrations of organic compounds such as hydroxyacids or amino acids would then require processes of evaporation of the ocean into which such compounds would fall. Such processes are visualizable as by the drying up of lagoons (Bernal, 1951).

In the second step, the only condensation that has been demonstrated in the context of our discussion is that of amino acids (Harada and Fox 1958; Fox and Harada, 1958). The polycondensation of glucose has, however, also been demonstrated (Mora and Wood, 1958). Both processes are carried out thermally in a remarkably similar range of temperature. The considerations discussed earlier do not permit the amino acid copolymerization either in a highly aqueous system or an anhydrous one, but rather in what can be referred to as a hypohydrous system containing perhaps 10–40% water. This in turn leads to a picture of a hot hypohydrous organic magma extruding into a marine or aquatic environment in the third step in which biological units result. It should be re-emphasized at this junction that the geological picture in the second stage is constructed for the only process that has yet been suggested to explain experimentally a material close to protein in nature. If any other process is invoked by successful experimentation, the geological picture will possibly be enlarged.

The conversion of a biochemical matrix to a first organism requires hydration in step 3 or before. Of all the assumptions exercised in visualizing the origin of life, perhaps the need for a predominantly aqueous system is the least likely to be questioned. When first proposed, the concept of modulation to an aqueous system during primordial formation of the cell raised a particular question. This is the one which stems from the known propensity of protein to be denatured in hot water. Part of the answer to this question is the information that the coagulation of protein is inhibited by small proportions of many substances, notable among which is nucleic acid, effective at such ratios as 1 nucleic acid: 100 protein (Greenstein and Hoyer, 1950; Hamer, 1954). A more convincing answer, albeit less specific, is simply that organisms live in hot springs. An additional thought is that surface denaturation of the protein in a globule of prebiochemical undergoing reaction could conceivably provide a primitive membrane for the cell.

The picture offered is an outline by which life could have originated.

It is subject to modification and improvement. In this all the thinking that properly composes organic geochemistry can undoubtedly find worthwhile exercise.

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Chapter 3

ORIGIN AND CLASSIFICATION OF NATURALLY OCCURRING CARBONACEOUS SUBSTANCES

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Organic geochemistry may be defined as the study of all naturally occurring carbonaceous substances. Inasmuch as the substances must be organic by definition, inorganic carbonates are automatically eliminated. On the other hand, an ill-defined region exists, such as in the case of carbonate shells formed by organic processes, where the carbonates certainly are products of organic processes and, therefore, are subject to study under the definition of organic geochemistry. Also to be considered are the roles played by organic processes in the redistribution and fixation of certain elements, in other words, the roles played in their geochemical cycles. This last consideration may very well turn out to be one of the most important, for little is as yet known as to the function of organic complexes in the formation of certain ore deposits of economic value. As examples, the formation of iron deposits may be cited, and reference may be made to the possible importance of organic complexes for the separation of iron and aluminum in the formation of bauxite deposits.

In view of the recent recognition by geologists of the potential importance of naturally occurring organic substances in geological processes, it is necessary that these substances be examined in considerable detail in order to establish a frame of reference for future studies. Also, inasmuch as it is quite clear that problems in organic geochemistry will be solved only by combined study by geologists, organic chemists, and physical chemists, it is of prime importance that a means of unambiguous communication be developed.

Nomenclature

The geological literature is replete with references to "hydrocarbon", the term used to describe any naturally occurring organic material. To chemists this implies a compound containing only carbon and hydrogen. It is hardly necessary to point out the ensuing confusion, for the reader can never be sure that the term "hydrocarbon" was used properly. Unfortunately, the literature almost never contains supporting analyses that could be used to clarify the problem.

When applied to geological occurrences, careless or indiscriminate nomenclature may have far-reaching consequences. Thus, use of a term such as "asphaltite" may connote an association with crude oil and give the reader a mental image that may never have been intended. In some instances this effect has even resulted in the development of exploration programs down fruitless avenues at great expense and with loss of valuable time.

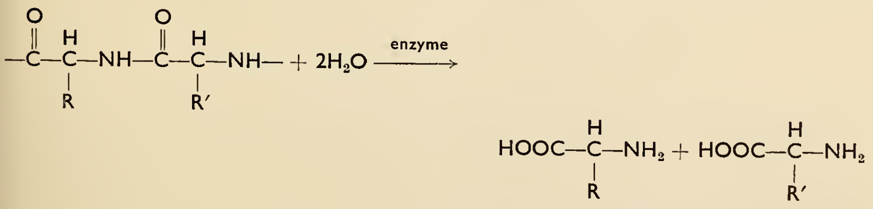
Many examples of such communication problems could be cited, and they all point to the necessity for a nomenclature that will satisfy both the field geologist and the investigator who works in the laboratory. The problem is complicated by the fact that the geologist, at times working under primitive conditions, is unable to do more than give the object he has collected a rather cursory examination. In view of the many possibilities for error under such conditions, it is advisable to use descriptive terms that are innocuous, such as "carbonaceous matter", rather than more specific names which may later prove, on closer examination of the sample, to be totally incorrect. More detailed discussion of nomenclature and classification of naturally occurring carbonaceous substances follows in a later section of this chapter.

Origin of Carbonaceous Substances

Of a number of approaches to the study of naturally occurring organic substances, the genetic route has without doubt provided maximum fundamental information. In this technique there are considered the progenitors, the depositional environment in which they were collected and preserved, and the effects of metamorphic agencies that cause secondary conversions leading to the products that are now found.

Progenitors

Proteins—Proteins, both the water soluble and water insoluble varieties, are composed of fewer than thirty different α-amino acids tied together in peptide linkages. Most proteins are sensitive to attack by proteolytic enzymes, such as pepsin or trypsin, which hydrolyze the peptide bonds to form partially decomposed proteins (Fig. 1). The latter are then attacked and degraded by other known enzymes. Proteolytic processes, which in effect hydrolyze the peptide bond, operate with but a slight energy requirement and serve to prepare the proteins for eventual utilization as energy



$$-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{\overset{H}{C}}-NH-\overset{\overset{O}{\|}}{C}-\underset{\underset{R'}{|}}{\overset{H}{C}}-NH- + 2H_2O \xrightarrow{\text{enzyme}} HOOC-\underset{\underset{R}{|}}{\overset{H}{C}}-NH_2 + HOOC-\underset{\underset{R'}{|}}{\overset{H}{C}}-NH_2$$

FIG. 1. Hydrolysis of a peptide bond.

sources in other oxidative or reductive biochemical processes. Although these processes and enzymes are those normally associated with human biochemical processes, there can be little doubt that analogous degradations occur in other animal systems. In general, these processes would be expected to result in the elimination of proteinaceous matter such as carbon dioxide, water, ammonia, nitrogen and hydrogen sulphide. Other labile products, such as urea, would, if produced, eventually yield similar degradation products.

Only in certain cases of putrefaction can biological processes result in the formation of stable nitrogen bases that might be incorporated into sediments. Examples of these processes are the formation of indole and skatole from tryptophan, cadaverine from lysine, and putrescine from arginine (Fig. 2).

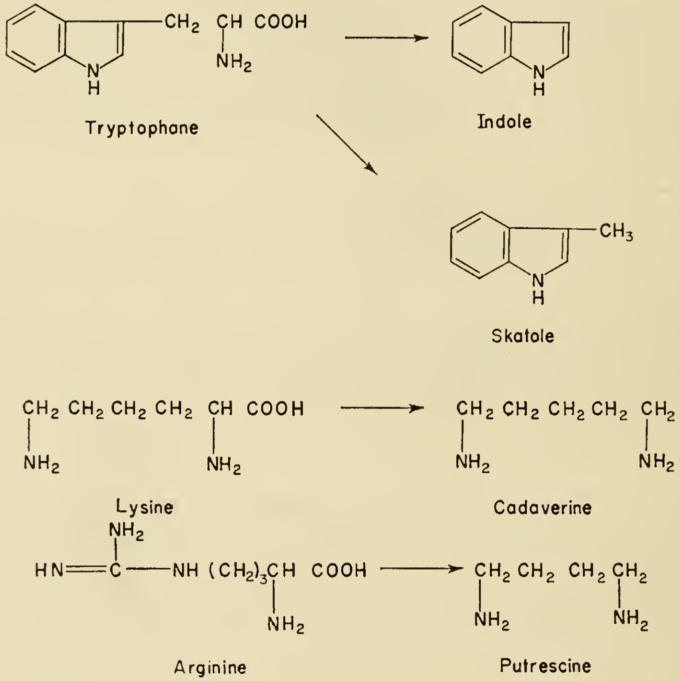


FIG. 2. Formation of nitrogen bases from amino acids.

Certain proteins of biological origin are associated with other compounds and are known as conjugated proteins. An example of such a compound is haemoglobin, in which the globin, a protein, is bound through imidazole nitrogen to protoporphyrin III containing an atom of reduced iron (Harper, 1957, p. 60) (Fig. 3).

It is evident that degradation of the protein will lead to a residue of porphyrin which, as evidenced by its occurrence in petroleum, shales, and coals, is resistant to biochemical decomposition.

Recent studies have shown that some amino acids survive in certain environments. Abelson (1957), for example, has been able to identify free amino acids in calcareous fossil shells. The minute quantities of such residual amino acids, however, attest only to a successful entrapment mechanism, but do not nullify the conclusion that proteins and their amino acids are labile, are biologically decomposed, and probably contribute very little to the overall picture in the genesis of organic deposits under geochemical conditions.

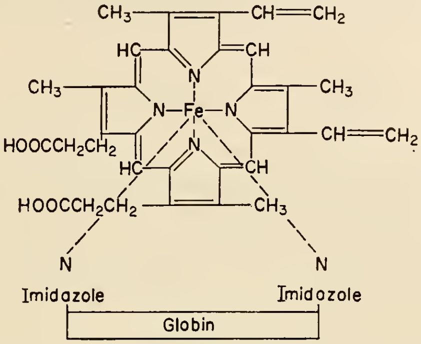


FIG. 3. Reduced haemoglobin (Harper, 1957).

Carbohydrates—Carbohydrates account for a major portion of both plant and animal residues. They are classified as saccharides or disaccharides, both of which are water soluble, some tri- and tetrasaccharides, and finally as essentially insoluble polysaccharides such as starch, cellulose, and glycogen. Monosaccharides are characterized as either polyhydroxy aldehydes or ketones; the formation of polysaccharides is accomplished by the elimination of water between the monomers to form oxygen bridges as shown in Fig. 4 for the disaccharide, cellobiose.

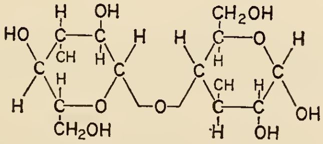


FIG. 4. Cellobiose.

Carbohydrates are subject to a great variety of enzymatic reactions that degrade them into simpler substances. Under anaerobic conditions fermentation can occur in which a six-carbon monosaccharide, glucose, is converted into alcohol without the addition of oxygen (Fig. 5). Other enzymatic processes are able to convert sugars into fat. As is well known, cellulose is bacteriologically ingested by herbivores and depolymerized into mono- and disaccharides that the animal can then metabolize as a source of energy. The enzymatic hydrolysis of carbohydrates is similar to the proteolytic degradation of proteins; in both cases the polymers are broken down into individual units or shorter chains with a minimum transfer of energy. The products of these reactions are subject to oxidation or reduction and are, therefore, sources of energy for life processes.

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{enzyme}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

FIG. 5. Conversion of glucose to ethyl alcohol.

In general, the final products of carbohydrate metabolism are carbon dioxide and water. Although the widespread disappearance of appreciable residues of carbohydrates is evidence of their sensitivity to biochemical degradation, there is some evidence that under certain conditions carbohydrates can be protected and can, therefore, survive through geological time. Vallentyne and Whittaker (1956) have recently found free sugars in lake waters and sediments, and Theander (1952) reported the presence of galactose, glucose, mannose, arabinose, xylose and rhamnose in hydrolysates from sphagnum peat. The presence of small quantities of cellulose in the Eocene brown coals of Germany has also long been known. The very fact that a careful search for these residual minute quantities of sugars has been necessary is in itself significant in demonstrating the rapid and nearly total degradation of carbohydrates.

Lignin—Lignin, although not a normal constituent of marine organisms, can nevertheless be a major contributor to organic deposits. Lignin has a phenylpropane structure and is an aromatic compound. It also has a flavonoid structure which, when opened, develops acidic properties. Using the Russell formula for lignin (Russell, 1948), not as an actual representation of the structure but merely as a guide for illustration of potential degradative reactions, it is possible to demonstrate such rupture as shown in Fig. 6.

The product illustrated is demethylated because the methoxyl content of lignin is known to decrease rapidly on degradation. Double bonds may also be formed by the dehydration of β-hydroxy ketones, and the resultant derivative of catechol is extremely reactive towards condensation reactions. Ring opening with attendant formation of a chalcone, as shown below, has been postulated to occur rather rapidly in the presence of dilute (0·12N) alkali (Fujise and Sasaki, 1938). Products of lignin degradation such as those shown must be considered in any conclusions regarding the fate of metabolic products in diagenetic environments.

Pigments—Pigments of various types are produced by plants and animals and should be expected to contribute to sediments in which organic substances are formed. These pigments are numerous in nature and variety but for the sake of brevity, only flavonoids, carotenes, and porphyrins will be considered. Examples of the first two types are shown in Fig. 7; the structure of protoporphyrin III has already been given.

In general, the percentages of these pigments in biological substances are quite low and it may well be for this reason that flavonoids and carotenes have rarely been identified in sediments, even if they survive.

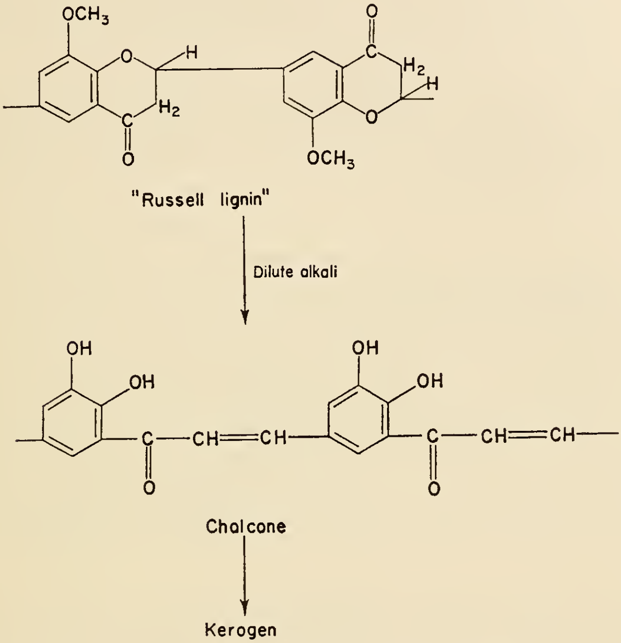


FIG. 6. Scheme illustrating the chemical conversion of lignin.

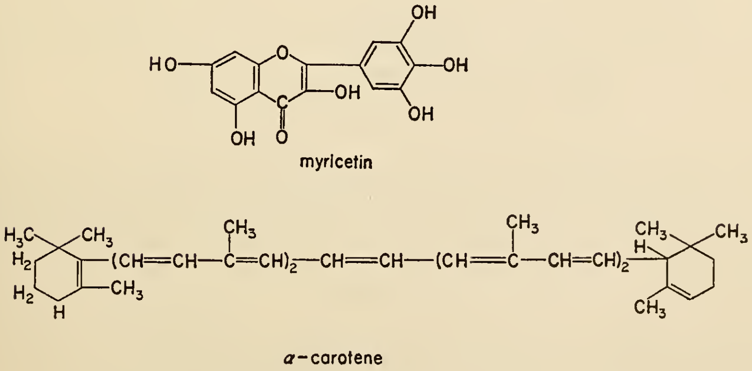


FIG. 7. Examples of flavonoid and carotenoid pigments.

Porphyrins, because of their high stability compared to other types of pigments, do survive and have been used successfully to demonstrate the low-temperature history of crude oil. Flavonoids, having the same basic structure as lignin, would be expected to hydrolyze to open-chain structures similar to those already discussed. Polyenes such as carotene, however, are extremely reactive and may well disappear by interaction with other substances or by intra- or intermolecular conversion. It may be noted in passing that β-carotene yields toluene, *m*-xylene, and 2,6-dimethylnaphthalene on heating at only 110°C. Degradation becomes understandable if the formula for β-carotene is written as shown in Fig. 8 (Kuhn and Winterstein, 1932).

Considering that minute quantities of amino acids and proteins have been found as residues of major biological products, it seems likely that residues of these pigments, which represent only minor products, will eventually also be identified.

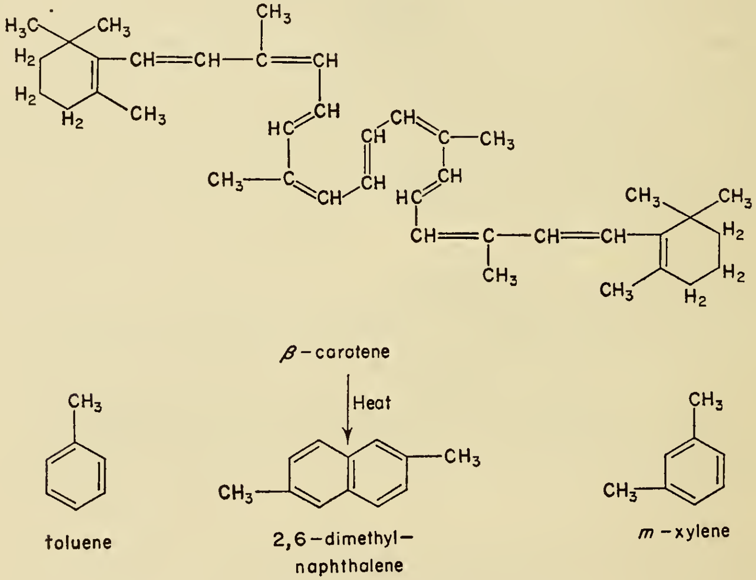


Fig. 8. Thermal degradation of β-carotene.

Lipids—To this point the discussion has covered proteins, carbohydrates, lignin and pigments; a consideration of lipids, which represents a third major biological product, has been left until last because of their particular importance.

Biochemically the term "lipid" refers to those substances that are insoluble in water but soluble in ether, benzene, or chloroform. They may be simple lipids, such as esters of fatty acids and alcohols, or of fatty acids with glycerol; compound lipids containing nitrogen, phosphorus, or sulfur; or derived lipids such as fatty acids, sterols or alcohols. For purposes of this discussion it is necessary to consider only the derived lipids inasmuch as many of the other varieties eventually break down to these simpler forms.

Natural glycerides, triesters of glycerol with various saturated and unsaturated fatty acids, disappear rapidly from depositional environments, presumably as a result of biological processes. Again, as in the case of proteins and polysaccharides, the glycerides are readily hydrolysable compounds yielding glycerol and fatty acids. The glycerol then serves as an energy source for biological processes, but the fate of the fatty acids, both saturated and unsaturated, is less well understood.

Fats and fatty acids are derived biologically from carbohydrates and amino acids. These reactions are dependent upon a two-carbon radical mechanism and, normally, give rise to even-numbered carbon chains. On degradation of a lipid then, there should be a preponderance of even-numbered fatty acids over those with odd numbers of carbon atoms in the chain. Saturated acids containing from four to twenty-six carbon atoms have been found in fats, but those with twelve, sixteen or eighteen carbon atoms are in the majority. Many unsaturated acids containing from one to six double bonds in unconjugated or conjugated positions are also known (Cowan, 1953). A number of fatty acids, ranging from formic to nonanoic, have been isolated from crude oil (Hancock and Lochte, 1939).

The fate of fatty acids in a marine environment is not well understood. Rosenfeld (1948) found that unsaturation decreased with increase in depth of burial, but that bacterial dehydrogenation also was quite general. No clear-cut evidence for direct biological decarboxylation of fatty acids has been noted.

Summary—From preceding discussion it appears most unlikely that carbohydrates or proteins contribute appreciably to the vast biomass of naturally occurring substances. There is evidence that small amounts of degradation products derived from carbohydrates and proteins may interact with other organic substances. In this manner some of the nitrogen of proteins may be introduced into the structure of coal, or may interact to form the quinolines and other nitrogen compounds found in crude oil. Sulfur derived from proteins or from the bacteriological reduction of sulfates may similarly be incorporated in the chemical structures of organic geochemical substances. Although it has occasionally been proposed that proteins and carbohydrates might be converted into other more complex and less well defined products, either through direct interaction, interaction of their degradation products, or even through interconversions without interaction, there is little or no valid evidence to support such suggestions. Moreover, the biochemical considerations already discussed restrict such possibilities.

Although pigments may not contribute appreciably to the geochemical biomass, they have, nevertheless, proved important as tracers for geochemical processes. Thus, as shown in Chapters 7 and 9, study of porphyrins has led to much fundamental information on the origin and thermal histories of coals, shales, and crude oil.

Lipids and lignin appear to be the most important organic substances in the formation of naturally occurring organic deposits. The fate of the lipids can be followed only in part, but these compounds may well be the progenitors of petroleum and asphalts (Breger, 1960).

Lignin, on degradation, does not undergo chain fission, as do proteins and carbohydrates, but remains intact as a long-chain product. This occurs in spite of the fact that heterocyclic oxygen rings may be hydrolysed in chemical or biochemical processes. The products from the initial degradation of lignin may be unsaturated and may also be related to phenols, especially resorcinol, in their chemical structure. It is obvious that such molecules, having a high degree of potential chemical reactivity, are capable of further conversions and interactions. Also, the phenolic character of the humic substances derived from the lignin has bacteriostatic properties that preclude any further appreciable biochemical degradation of the material. The relative sterility of peat has long been known and was effectively demonstrated by Barghoorn (1949), who reported the absence in peat of sulfate-reducers and other anaerobes. Concentration of large masses of humic material derived from lignin is known to result in the formation of coal; recent studies on marine carbonaceous shales have also shown that the organic matter of these rocks is primarily derived from terrestrial sources and, therefore, from lignin (Breger, Tourtelot, and Chandler, 1961; Breger and Brown, 1962). Inasmuch as carbonaceous shales and coals account for the overwhelming proportion of the geobiomass, it is clear that lignin must be the major contributor to that mass.

Detailed studies of the degradation of wood under geological conditions have provided much evidence for the course of the decomposition. Thus, Barghoorn (1949), Varossieau (1949), and Varossieau and Breger (1951) noted the concentration of lignin-like residues and the loss of cellulose when wood is buried under anaerobic conditions. Pentosans were found to be relatively resistant to decomposition. Also, the loss of cellulose is not always predictable, and varies between one portion of a plant and another, even in different parts of the same portion of the plant.

The acidic nature of the lignin molecule on initial degradation is demonstrable in old buried wood (Varossieau and Breger, 1951) where loss of methoxyl content is related to increase in extractability of acidic products. This is thought to represent the initial stage in humus formation and, therefore, in the formation of soil organic matter or coal.

From the above discussion, it must be concluded that all organic products that undergo geological preservation apparently are subject to more or less degradation. It must, however, also be recognized that small quantities of some of these substances may, through entrapment, be preserved and survive the normal degradative process thereby contributing an odd product to the ultimate geobiomass.

Metamorphic Processes

Barghoorn (1952) pointed out that coal "is a biological and geological accident resulting from minor inefficiencies in the microbiology and biochemistry of the Carbon Cycle". This statement can be extended to include any biomass if the microbiological inefficiencies are supplemented or replaced by diagenetic influences. Where some substances, such as humic materials, are acidic and affect microbiological influences through establishment of local environment, other substances may accumulate through entrapment in an unusual environment of deposition. Thus, microbiology, environment of deposition, and finally diagenetic factors all may, and frequently do contribute to the ultimate fate of an accumulating biochemical.

Among the metamorphic processes that are or may be effective in the diagenesis of organic substances are those of a microbiological character, chemical reactions, heat, catalysis, pressure, and time.

Microbiological factors—The microbial degradation of proteins and carbohydrates has already been discussed, and it was pointed out that these substances are prone to enzymatic degradation. Innumerable organisms, both aerobic and anaerobic, are known that attack and utilize these substances as energy sources. Fungi, aerobic and anaerobic bacteria, and other microorganisms all attack and destroy carbohydrates and proteins. Although the range of organisms that attacks lignin is not nearly as broad, significant changes in lignin structure are brought about to give that substance new physical and chemical properties. Thus, it was proposed (Breger, 1951) and subsequently demonstrated (Pommer and Breger; 1960a, 1960b) that the degradation of lignin and its conversion to humic acid gives that substance acidic properties and yields products of undoubtedly lower molecular weight than existed in the original plant.

Microorganisms also play a significant role in the degradation of organic debris from aquatic sources. The products derived from plankton, diatoms, algae, fish, and other aquatic life-forms are subject to biochemical decomposition on the floor of a marine or non-marine environment. Under these conditions, carbohydrates and proteins are very likely hydrolyzed and utilized thereby contributing but little to the residual organic deposit. Lipids are probably converted into water-soluble glycerol and a mixture of polyunsaturated fatty acids, which may be important progenitors for petroleum hydrocarbons (Breger, 1960).

Initial microbial degradation of organic debris, either on land or under water, must be very rapid. As substrate is decomposed, the capacity of the material to support additional attack appears to drop rather rapidly, especially if the nature of the residues, as in the case of humic acid from lignin, is such as to depress continued attack. This was demonstrated by Varossieau (oral communication, 1950), who found that buried, degraded wood was able to support only a limited population of thermophilic bacteria.

The literature on microbial attack of organic residues under geochemical conditions is extremely extensive but very widely dispersed. Agricultural experts have studied the microbial populations of soils intensively and much fundamental work was summarized by Waksman (1936). More recently, Beerstecher (1954) recorded available information on the importance of microorganisms in various aspects of the petroleum industry.

Chemical factors—Although hydrolysis of plant and animal constituents, such as proteins and carbohydrates, may occur during microbial attack, it is still possible for such reactions to take place in a sterile environment. Addition of the elements of water to a peptide linkage or to a polysaccharide will also hydrolyze these compounds under sterile conditions. Thus, the disaccharide, (+)-maltose, is converted to the monosaccharide D-(+)-glucose either by aqueous acid or by treatment with the enzyme maltase obtained from yeast (Fig. 9).

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow 2\ \underset{\text{glucose}}{C_6H_{12}O_6}$$

FIG. 9. Conversion of maltose to glucose.

Varossieau (1949) had noted that there was little evidence for microbial attack on wood buried for hundreds of years in water-impregnated sand; further observation showed that these logs had not been attacked by fungi. Loss of cellulose and other wood constituents were, therefore, attributed to purely chemical hydrolysis. Barghoorn (1949) also questioned the relative roles of microorganisms and chemical processes in the alteration of plant remains and concluded that not all transformations need be attributed to the effects of organisms. There is no reason to preclude purely chemical hydrolysis of certain compounds given the proper pH and sufficient time. It has already been suggested that the benzopyrone structure of lignin may be opened chemically by dilute aqueous alkali to yield constituents of humic acid. This may be the explanation for the origin of the acidic products apparently derived from lignin in logs buried in sand under water (Varossieau and Breger, 1951).

Oxidation of organic deposits can occur either under terrestrial or shallow aquatic conditions. Occasionally evidence has even been obtained to show that oxygen can be carried into deep marine basins and bring about oxidation under the most unlikely conditions. All organic substances are subject to more or less oxidation, and the accumulation of an organic deposit attests to the fact that the conditions during storage must have been primarily reducing.

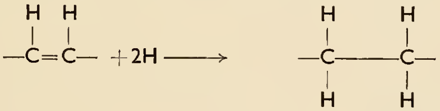
Oxidation is synonymous with combustion, and the prolonged exposure of most organic substances to oxygen will eventually lead to their conversion into carbon dioxide and water. Breger and Brown (1962) have shown, however, that even the relatively resistant humic substances from terrestrial plants may be partially oxidized before burial and accumulation in a reducing environment. This oxidation probably occurred in shallow water close to the shoreline of a barred marine basin where wave action may have led to some oxidative degradation of the material prior to its entrapment in the underlying reducing environment.

Attack by oxygen on an organic substance can take two routes. Under most conditions and with most substances, the oxygen combines with the organic material to yield a product containing an increased percentage of oxygen; with other substances, where the introduction of oxygen into the molecule cannot be accommodated, oxidation leads to the removal of hydrogen and to a product enriched in carbon. An example of oxidative dehydrogenation is to be found in asphaltic substances where neither natural nor artificially prepared asphalts are able to absorb more than about 3% of oxygen by weight. Beyond this limit, treatment with oxygen leads to loss of hydrogen. This loss of hydrogen may in turn lead to molecular unsaturation which, in the presence of oxygen and peroxides, results in polymerization of the molecules. Colombo (personal communication, 1961) has suggested that many viscous asphalts that occur as seeps may have originated from stripped crude oil by this mechanism.

The indirect effects of oxygen on the metamorphism of organic substances are not always easy to evaluate. Under aerobic conditions attack by fungi, aerobic bacteria, and other microorganisms is promoted. Hydrolysis followed by destruction of molecules is undoubtedly the major effect of this attack, but little is known about other possible reactions that may occur.

Much evidence points to the fact that hydrogenation (reduction) of organic substances must occur under reducing geochemical conditions. The formation of hydrocarbons from oxygen-containing compounds may be considered to be a reduction in the same sense that oxidation and dehydrogenation are equivalent.

Although the virtual absence of hydrogen in natural gas has been explained on the basis of loss through diffusion, there is no doubt that hydrogen produced during biochemical reactions can be absorbed chemically to reduce unsaturated bonds in organic molecules (Fig. 10).



$$-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}- + 2H \longrightarrow -\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-$$

FIG. 10. Absorption of hydrogen by unsaturated bonds.

This reaction would not only remove hydrogen from natural gas, but would also account for a decrease in unsaturation of organic deposits.

The effectiveness of or necessity for catalysts in the hydrogenation of organic substances under natural conditions has not been evaluated; availability of hydrogen atoms will, of course, make a catalyst unnecessary.

The role played by catalysts in organic geochemistry is not well understood. With the introduction of catalytic cracking processes in the petroleum industry prior to the Second World War, an attempt was made to extrapolate catalytic activity to geochemical environments. Brooks, in a number of interesting and provocative articles, suggested that acid silicates, particularly clays, are effective in the polymerization, isomerization, and hydrogen disproportionation of natural hydrocarbons (1954). Extension of refinery practice to natural conditions has not been completely satisfactory inasmuch as relatively high temperatures have been employed in laboratory experiments, and because most clays and other potential silicate catalysts tend to occur in a non-acidic form. Recently Zkhus (1958) suggested an entirely different role for clay minerals in the formation of crude oil. Instead of considering the catalytic effects of the clays, this author suggested that the conversion of montmorillonite to hydromica is accompanied by the release of sufficient energy for the conversion of complex organic compounds into petroleum hydrocarbons. So little is known regarding the thermodynamics of clay minerals, however, that it is difficult to evaluate this suggestion.

This association of vanadium with certain asphaltites (Fester and Martinuzzi, 1948) led to the suggestion that this element may have promoted catalytic oxidation or polymerization of the material. Here, too, there is no supporting evidence for this view.

Although it has frequently been suggested that catalysis plays an important function in organic geochemical processes, no unqualified positive or negative supporting evidence has as yet been advanced.

As has already been noted, there can be no doubt but that some intermediate degradation products of organic substances may interact chemically with similar products from another source. The occurrence of nitrogen in coal and crude oil points toward proteins, or amino acids derived from them, as chemical reactants with the coal-forming substance or with the progenitors of crude oil. Degradation of woody plants may also lead to intermediate products derived from cellulose, such as aldehydes or ketones, which may react chemically with the lignin degradation products. Barghoorn (1952a) suggested than an appreciable fraction of such cellulosic residues may remain in organic sediments, undergoing conversion to other compounds. While this may be so, evidence in favor of such a source of organic residues is difficult to obtain, and cell fillings in coalified wood may actually be derived from humic substances formed during the decomposition of lignin.

The interaction of carbonyl groups, such as those of sugars, with amino groups, such as those of amino acids and proteins, is well known as the Schiff Reaction (Fig. 11). This reaction, which creates a new carbon–nitrogen bond, takes place readily in aqueous solution under alkaline conditions, and may account for the introduction of nitrogen into coals and petroleum.

$$\mathrm{RCHO} + \mathrm{H_2NR'} \longrightarrow \mathrm{RCH{=}NHR'} + \mathrm{H_2O}$$

FIG. 11. Example of the Schiff Reaction.

Many other chemical reactions are possible and may be suggested to explain possible organic interactions. Among such reactions is that known as the Diels–Alder Reaction which is illustrated in Fig. 12. The R in this case usually represents an activating carbonyl (>C=O) group. As an example, the interaction between eleostearic acid from tungoil, and crotonic acid, would be expected to yield cyclic products (Fig. 13).

As a further example of the many compounds that can be derived through Diels–Alder Reactions, the interaction between cyclopentadiene and maleic acid to give a bridged product is illustrated (Fig. 14).

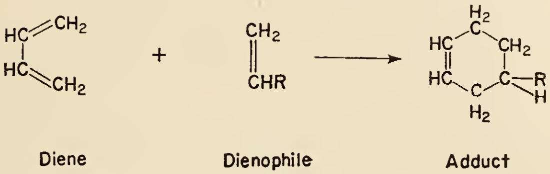


Fig. 12. Example of Diels–Alder Reaction.

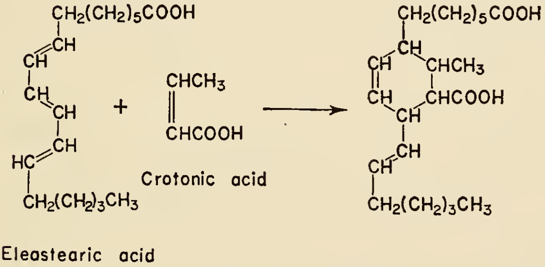


Fig. 13. Example of a Diels–Alder Reaction showing one of several possible products obtainable from eleostearic and crotonic acids.

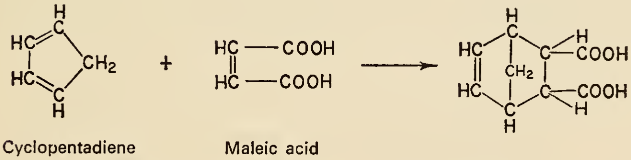


Fig. 14. Diels–Alder Reaction between cyclopentadiene and maleic acid.

The Diels–Alder Reaction is a purely chemical process operative at normal or elevated temperatures. This reaction can take place in hydrous media as shown by Sowa (1951), who found that α,β-unsaturated acids react readily with conjugated dienes at pH values below 7. This reaction may take on further importance in view of the recent discovery that it is catalyzed by aluminum chloride or other acid catalysts (Fray and Robinson, 1961). Under a wide variety of conditions a broad spectrum of partially unsaturated ring compounds might be expected to result from the Diels–Alder Reaction. Hydrogenation to alicyclic compounds or dehydrogenation to aromatic compounds is not inconceivable. Decarboxylation of adducts formed from unsaturated fatty acids, along with hydrogenation or dehydrogenation, might well account for the formation of cyclic, aromatic, bridged, or mixed-type hydrocarbons such as occur in crude oil (Breger, 1960).

The similarity of products, such as 2,6-dimethylnaphthalene, derived on thermal degradation of β-carotene (page 56) to those which might be obtained through a Diels–Alder Reaction is worth noting. The carotene, in this case, would serve as both diene and dienophile.

It is quite evident that many chemical reactions can be hypothesized to account for interactions between organic species under geochemical conditions. The above discussion of the Diels–Alder Reaction has been given particular emphasis because of its potential importance in the origin of petroleum, but other reactions may be equally important. As an example, Pommer and Breger (1960b) suggested the interaction of carbonyl groups and alcohols to form hemiacetals under acidic conditions (Fig. 15), and even presented evidence for aldol condensations between carbonyl-bearing compounds in alkaline environment with the formation of β-hydroxy carbonyl or α,β-unsaturated carbonyl compounds (Fig. 16).

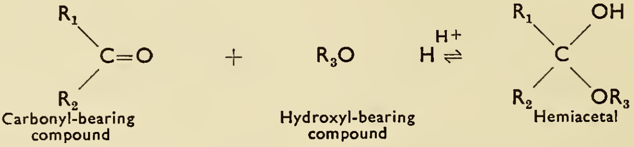


FIG. 15. Formation of a hemiacetal.

Unfortunately, studies of this type related to geochemical conditions are difficult to organize, and the results are rarely unambiguous. For these

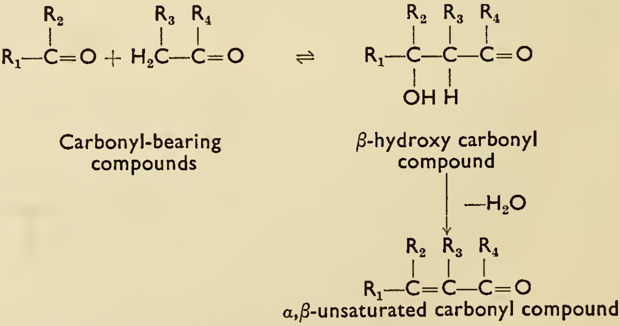

R₁—C=O + H₂C—C=O
R₂ R₃ R₄
⇌
R₁—C—C—C=O
OH H
Carbonyl-bearing compounds
β-hydroxy carbonyl compound
—H₂O
R₁—C=C—C=O
α,β-unsaturated carbonyl compound

FIG. 16. Example of an aldol reaction.

reasons, organic interactions under geochemical conditions have hardly been studied.

Physical factors—Radioactivity has, on several select occasions, been shown to bring about diagenetic changes in organic geochemicals. The association of uranium with coalified logs on the Colorado Plateau has led to radiochemical dehydrogenation of the coal (Breger, 1956; 1961). Humic extracts derived from coal have also been crosslinked and polymerized to insoluble forms by radiochemical mechanisms (Breger and Deul, 1959). In such instances, the energy for the radiochemical reaction undoubtedly comes from the alpha particles emitted by the uranium and, especially, its daughter products. These charged helium atoms, because of their high mass, carry approximately 75% of the energy associated with radioactive decay.

Occurrence of uranium with organic substances is fortuitous, depending upon a source of uranium, a transport medium, and an organic acceptor substance. Inasmuch as most organic substances appear to be excellent acceptors, the critical part of the chain lies in the availability of uranium. The occurrence of unusually high amounts of uranium only in certain provinces, and its general absence in quantities sufficient to effect radiochemical reactions, point to the unimportance of radioactivity as a general diagenetic agent.

Thermal factors—Increase in temperature of 10°C will normally double the rate of a chemical reaction. For this reason, thermal effects can be extremely important in promoting diagenetic changes in organic compounds. Compounds of low molecular weight may distill, but those complex substances that are not volatile are subject to thermal degradation at a rate dependent upon the temperature to which they are exposed.

Measurement of geological temperatures is not always easy, nor is it always possible to extrapolate back in time to estimate the temperatures that once prevailed. For these reasons, it is commonly not possible to relate changes that have occurred in organic substances to thermal effects.

In some instances thermal degradation of organic substances is obvious. Thus, penetration of coal seams by dikes generally leads to alteration of the coal in zones up to about one foot on either side of the intrusion (Clegg, 1955). Such localized coking is easily discernable.

Authenticated examples of thermal degradation of organic substances followed by distillation of the tars and other volatile products formed are practically non-existent. In spite of the fact that this mechanism has frequently been proposed to account for geological occurrences of organic substances, only one well-documented case of *in situ* distillation is known.

Mueller (1951) has shown that dikes cutting a carbonaceous shale in Derbyshire, England, led to decomposition of the organic matter and intrusion of the distillates into voids in the sediment. An interesting aspect of Mueller's study is that the organic distillates were apparently segregated into aliphatic and aromatic products, each type of which may have formed at a different temperature during the heating process. This would be in keeping with the fact that pyrolytic products from coals or shales differ in composition depending upon the temperature of distillation.

Such obvious thermal effects are easy to define, but it is much more difficult to evaluate thermal changes in an organic deposit brought about by prolonged low-level heating. Exposure of a coal bed or a carbonaceous shale to an increase in temperature of 20° to 30°C for several hundred thousand or million years may result in slight but, nevertheless, appreciable changes in the organic matter.

Apart from extraordinarily high temperatures caused by dikes, sills, or other igneous flows, most geological temperatures associated with organic substances appear to be in the geothermal range. Bottoms of some oil wells have been reported to be extremely hot, up to 200°C, but normally the temperatures correspond to the geothermal gradient, i.e., about 1°C/100 ft. Thus the bottom of a 7000 ft hole would be expected to be at 70°C plus 20°C for estimated surface temperature, or at 90°C. This certainly is not an unusually high temperature. Taking advantage of a set of limited conditions, Breger and Chandler (1960) studied the *in situ* extraction of coalified logs from the Colorado Plateau to determine the temperature at which the extraction occurred. Conclusions reached from this work pointed to 120°C at the maximum temperature to which the logs were exposed, a temperature also deduced from geological evidence that overburden in the region had once amounted to about 10,000 ft of sediment. It is interesting that these particular diagenetic changes in the coalified logs could be directly related to temperatures at which the changes occurred.

Other organic compounds have also been used in geothermometry because of their sensitivities to thermal degradation. The carboxyl groups of certain porphyrins are lost rapidly above 200°C. Isolation of the carboxylated porphyrins from crude oils, coals, or shales has, therefore, been taken as evidence that the specimens were never exposed to temperatures above 200°C. Limitations imposed on the thermal history of these substances have been critical in understanding their origin.

High pressures are frequently called upon to account for metamorphic changes in organic substances. As in the case of temperature, however, the effects of pressure are very frequently difficult to evaluate and may either be overestimated or overlooked. Moreoever, there appears to be a great difference between the effects of hydrostatic pressure and shear.

As early as 1914 Bridgman reported egg albumin to be coagulated by hydrostatic pressures of 5000 to 7000 atm applied over a period of thirty minutes. It was not until 1929 that Bridgman and Conant extended the original study with a series of investigations on many types of organic compounds. Pressures of 10,000 atm exerted over a period of 24 hr were found to have no effect on amylene, pinacone, tertiary amyl alcohol, diacetone alcohol, and other substances; almost the same conditions, however, led to the partial polymerization of isoprene, 2,3-dimethyl-1,3-butadiene, styrene, and indene. Isobutyraldehyde and *n*-butyraldehyde were converted to soft, waxy solids under pressures of 12,000 atm exerted for 40 hr. In this and a later paper (Bridgman, 1946), polymerization was attributed to the presence of peroxides in the compounds under investigation. These are the first reported examples of irreversible chemical transformations cause by hydrostatic pressure.

In 1939, Raistrick and co-workers found that cyclopentadiene polymerizes in three stages under pressures up to 5000 atm and at temperatures of 0° to 40°C. It was specifically found that dimerization takes place first and is then followed by the production of higher polymers. An explosive disruptive reaction took place within definite pressure limits at each temperature resulting in the formation of a carbonaceous residue and much gas (92% methane and 8% hydrogen). An important observation by Raistrick was that the carbonaceous residue had an X-ray structure similar to that of low-temperature coke obtained from coal at 550°–600°C.

Further polymerization studies were carried out in 1945 by Vereshchagin and Polyakova, who found that cyclohexadiene polymerizes at 300° to 360° under 4000 atm, but that the polymerization is independent of pressure. The polymers which were produced were found to be identical with those formed thermally. The polymerization of vinylcyclohexene, on the other hand, was reported to be pressure-dependent at 250°C. The occasional interconvertability of different sources of energy, namely heat or pressure, is exemplified by these studies. On the other hand, it must also be remembered that other possible factors, such as the effects of peroxides, may tend to obscure and simplify the picture.

It is interesting to note the results of experiments by Johnson and Lewin (1946) in which *B. escherichia coli* were subjected to pressures up to 8000 lb/in^2. These investigators found that a pressure of 1000 lb/in^2 retards the growth of the bacterium, while 5000 lb/in^2 causes disinfection or bacteriostasis. At temperatures above the optimum for the growth of the bacteria, a pressure of 1000 lb/in^2 has an opposite effect and actually accelerates growth. This work may offer a clue as to the importance of bacteria in compressed sediments.

Much work has been reported with respect to the effects of high pressures on proteins and enzymes (Bridgman, 1946), but the results of these experiments are difficult to interpret. Libby, in an oral paper delivered before the National Academy of Sciences (1962), again demonstrated the denaturation of proteins when exposed to high pressures.

Several Bulgarian workers have described experiments in which they subjected coal samples to hydrostatic pressures in the range of 10,000 atm. Analysis of coke yields and of tar fractions before and after the application of pressure indicated that a small but significant structural change in the coal material must have taken place as a result of the compression (Trifonow and Toschew, 1939, 1940; Trifonow and Phillipow, 1941).

A very significant series of experiments was reported by Bridgman in 1935 in which samples of organic and inorganic materials were compressed to pressures up to approximately 50,000 atm and then sheared to the point of plastic flow. Many substances such as graphite, sugar, rosaniline, or rochelle salt underwent no change as a result of this treatment. Rubber, Neoprene, wood, paper, and linen cloth, however, were changed to horn-like substances which were, in some cases, translucent. When celluloid or iodoform was placed under a hydrostatic load of up to 50,000 atm, no chemical changes were observed. When sheared under this pressure, however, both substances decomposed explosively.

These experiments emphasize the fact that it may be possible by shearing complex substances, under the proper conditions, to cause the cleavage and re-formation of chemical bonds thereby producing a new type of compound without the use of high temperatures.

The effects of pressure have, perhaps, been most thoroughly studied with respect to the metamorphism of coal. One of the oldest attempts to explain coalification was that by Hilt (1873) who hypothesized a correlation between depth of a coal seam and its increased carbon content. In two very significant papers, Trotter (1952, 1954) noted a lack of any such relationship in several coal fields.

Other attempts to relate pressure to increase in rank led R. and M. Teichmüller (1947) to conclude that pressure is effective in changing the rank of coal only when it is transformed into the heat of friction. That shear forces are important in the formation of bituminous coals and those of higher rank has long been suggested (Kreulen, 1948, p. 37), but it is not known if heat accompanying the shearing action, as suggested by the Teichmüllers, or the action itself is the important factor in bringing about the chemical changes. In view of that fact that thermal treatment of coal (Van Krevelen, 1950) does not lead to changes in composition falling consecutively on the normal coal curve (Seyler, 1948), it would appear that shear force is more important than the effects of any accompanying evolved heat.

It might be noted that burial, as in the case of a coal seam, is normally accompanied by the sagging of strata such as occurs in a syncline. If shear is critical in inducing the chemical changes in coal that are measured by increase in rank, then the extent of sag of the sediments might be of extreme importance, for depth of burial in the syncline will be related to increase in the degree of shear. It appears unlikely that thermal effects alone could cause the changes noted as coal rises in rank.

In study of the effects of pressure and temperature on lignin, Breger (1950) found that under shear, at 100°C, and when loaded to 1655 atm, the methoxyl content of the material was reduced by about 0·5 percent as a result of the piezochemical action; heat and hydrostatic pressure alone caused no such change.

An interesting approach to coal metamorphism was made by Szádeczky-Kardoss (1952), who compared diagenetic changes in clays and other rocks with those for coals. Basing his calculations on maximum temperatures for coalification taken from the literature, he derived a relationship in which an increase in temperature of 1°C was equivalent to the application of a pressure of approximately 33 atm. In view of the foregoing discussion, it is difficult to evaluate such an interrelationship without specifying whether the pressure is purely hydrostatic or is confining while the sediments are being sheared.

The potential importance of shear in the possible conversion of insoluble organic matter (kerogen) of carbonaceous shales into petroleum hydrocarbons was considered during early studies of the origin of petroleum. Experiments in which samples of confined shale were sheared led to the conclusion that no significant geochemical changes had occurred and that no hydrocarbons had been produced (Hawley, 1929).

It should be quite obvious that hydrostatic pressure alone should bring about no appreciable changes in those compounds that are thermodynamically stable. Thus, there is no reason to expect changes in the hydrocarbons of petroleum, unless the confining pressure serves to retain the compounds while they are subjected to thermal changes. Compounds that are relatively unstable may interact, however, as when egg albumin is subjected to high hydrostatic pressure. Shear, on the other hand, may provide sufficient energy to break certain bonds in solid materials, and these unstable intermediates may then interact to form new, more stable compounds of higher molecular weight with elimination of energy as the new bonds are formed. Thus, the difference between that energy imposed upon the system to bring about the reaction, and that released during reaction, may be very small. It is possible that coal is metamorphosed from lignite to anthracite in this way, and that the ultimate rank of the product is dependent upon the imposed degree of shear.

There have been very few objective geochemical studies from which to evaluate the effects of pressure and temperature on organic substances. This is a field of investigation that requires additional attention.

Time, as a metamorphic factor, can be evaluated only in terms of a few limited geochemical observations. As examples can be cited the fact that coalified logs ranging in age from those of the Upper Devonian to those of Triassic, Jurassic, and Cretaceous age, when buried in shales, sandstones, or arkoses, all reached the same general coal rank, namely, subbituminous to high-volatile bituminous. The inference to be drawn is, of course, that time has not been a metamorphic factor once the coal reached its ultimate composition (Breger and Schopf, 1955; Breger, 1956, 1961). The recent conclusion that most of the organic matter, called kerogen of the Upper Cretaceous Pierre and Upper Devonian Chattanooga Shales is both related to coal and is of approximately the same "rank", in spite of differences in age, provides confirmatory evidence that time alone is not an important metamorphic factor, at least insofar as coal is concerned.

With substances that are chemically more reactive than coal, such as asphalts, it is possible that a kinetic factor is important. Thus, the formation of the so-called anthraxolite associated with the Little Falls diamonds of the Upper Cambrian and Lower Ordovician dolomites of New York (Dunn and Fisher, 1954) may represent continuous metamorphism dependent upon time, or may on the other hand be related to the silicification process. It is difficult to isolate all potential causes in such a complex system.

Although organic geochemicals may be derived from many sources, the ultimate metamorphic products are graphite or diamond. In between the progenitors containing predominantly carbon, hydrogen, oxygen, and nitrogen, and the ultimate carbon, there may be a number of metamorphic branches in which, under the conditions of preservation, certain thermodynamically stable intermediate compounds tend to accumulate. The hydrocarbons of crude petroleum may represent such a metamorphic branch, just as do the small quantities of so-called organic minerals or mineraloids represented by the anthraxolite discussed above and by numerous other substances, such as gilsonite, descriptions of which have occurred frequently in the literature. In general, most organic substances tend to approach graphite in ultimate composition. The occurrence of diamonds in meteorites or in volcanic necks representing metamorphism that occurred under conditions of extraordinarily high temperature and pressure.

That graphite is the stable form of carbon produced under most geochemical conditions is clearly evident. Organic matter of the Precambrian Grenville series of northern New York and Ontario has been reported to be graphite, and that of Precambrian phyllites of the Quadrilatero Ferrifero of Minas Gerais, Brazil, although containing only 96% carbon, nevertheless shows a highly graphitic X-ray pattern. Coal, too, with increase in rank from bituminous to anthracite, exhibits a continuous increase in graphitic structure.

If metamorphism of various organic geochemicals, with but few exceptions, results in the same ultimate product, it is obvious that analysis of that product may be of little or no value in ascertaining the material from which it was derived and the metamorphic factors that influenced its formation. Rate of metamorphism is also critical as can be demonstrated by reference to Fig. 17.

Starting with five organic substances at time T_0, and following their compositional changes as they undergo metamorphism, it is possible to consider their ultimate conversion to graphite at T_u, ultimate time, by two metamorphic sequences. In Scheme I, each of the five substances undergoes continuous linear degradation with time, whereas in Scheme II, the same five progenitors undergo rapid degradation at first, after which their rates of degradation become more gradual. Referring to both schemes, it is evident that even at the time designated as T_1, there are sufficient differences in the compositions of the five substances so that it may be possible to differentiate them and learn something about their respective origins. At T_2, however, differentiation of the substances being metamorphosed by Scheme I may still be possible, whereas the compositions of the same metamorphic products in Scheme II are now so similar that extrapolation to their origins may by this time become extremely difficult or even impossible. The situation at T_2, comparing the two schemes, becomes even more acute with increasing time. It is clearly evident, therefore, that rate of metamorphism may be an extremely important factor in comparing the origins and histories of organic geochemicals.

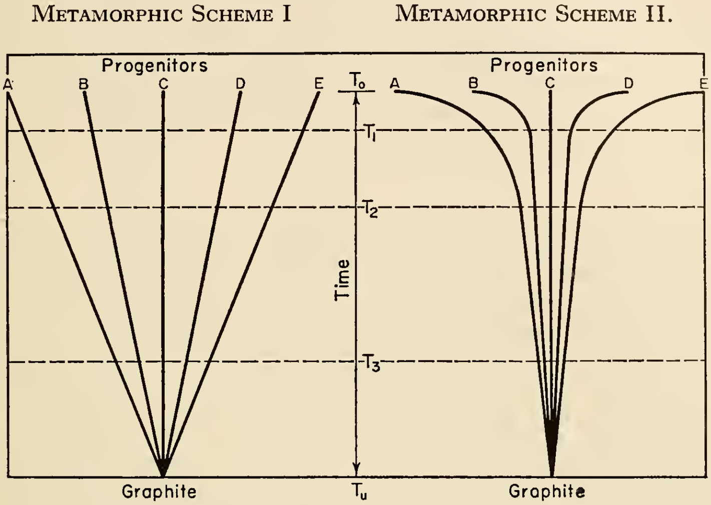

METAMORPHIC SCHEME I METAMORPHIC SCHEME II.

FIG. 17. Schematic representation of diagenetic processes.

Most organic compounds undergo rapid and extensive biochemical changes once they are deposited in geological environments. After initial degradation, metamorphism may be very slow or may even cease. As an example, the organic progenitors of coal pass through a rapid biochemical phase of decomposition which leads to the formation of peat, lignite, subbituminous or high-volatile bituminous coal. Thus, wood may be converted into coal having approximately 84–85% carbon. The product of the biochemical metamorphism may undergo no further appreciable changes, other than perhaps those accompanying mild compaction and colloidal phenomena, and may remain as such over long periods of time. The example of wood buried in shales (Breger and Schopf, 1955) has already been cited to illustrate this point. Further chemical conversion of coal takes place only when it is subjected to external physical forces; this is known as the dynamochemical phase of metamorphism and, although it may cause profound changes in the physical properties of the coal, it is not as a rule accompanied by the great compositional changes that occur in the biochemical phase of metamorphism. This is illustrated in Metamorphic Scheme II, where the biochemical phase is essentially complete in time T_2, and where further compositional changes, which are relatively small compared to those that occur between T_0 and T_2, are the result of dynamic factors, such as pressure.

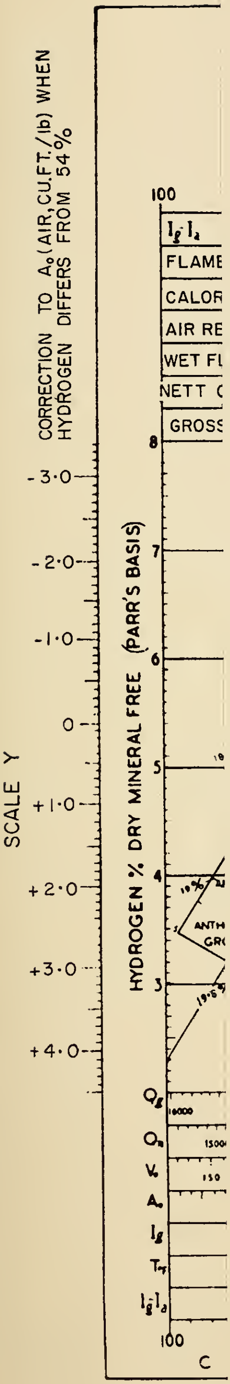
Carbon content is used as an index of metamorphism in Fig. 17, but other indices, if sufficiently sensitive, may be equally useful. Thus, hydrogen content, plasticity, or even particular infrared spectral absorptions may be used in evaluation of metamorphism.

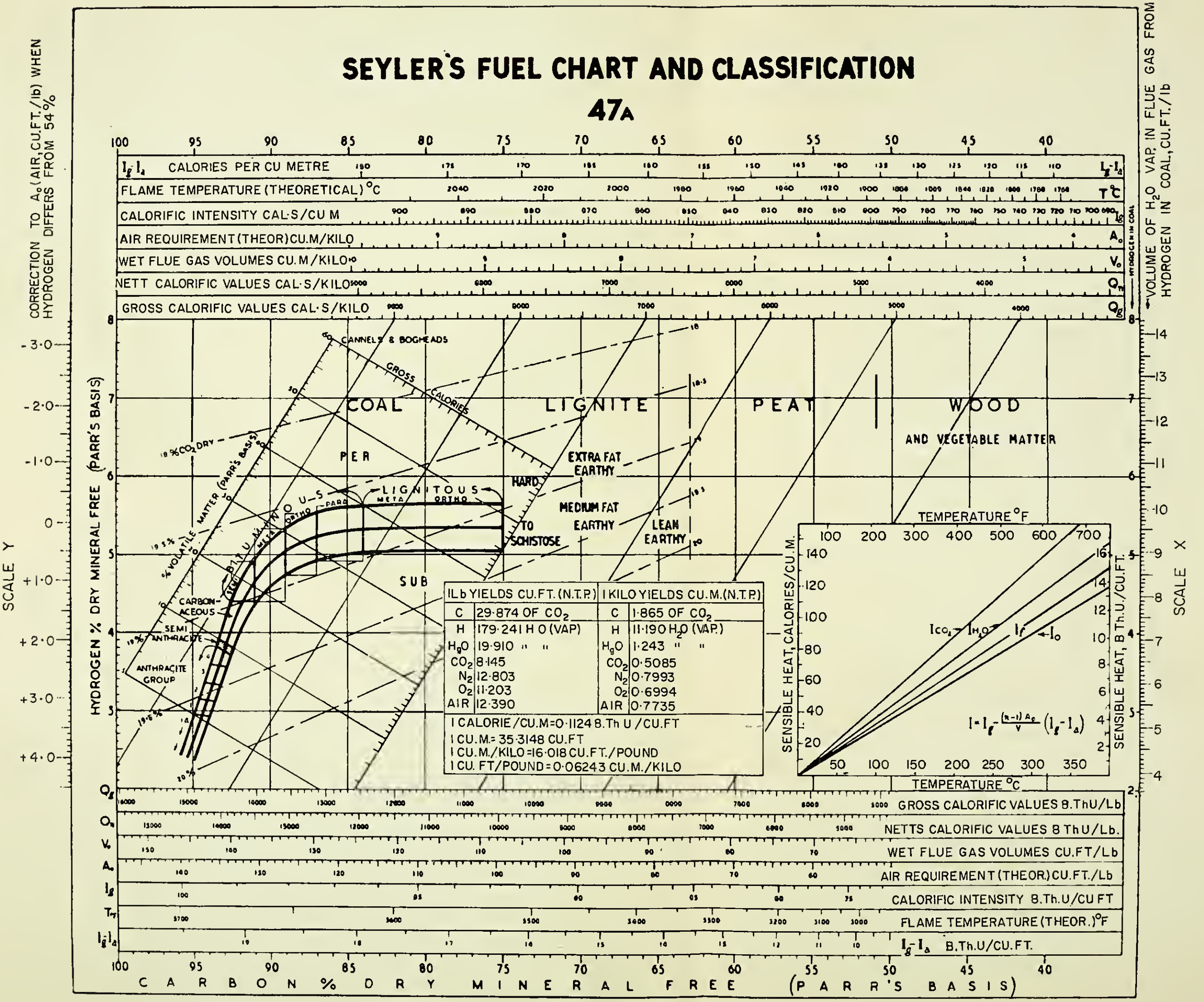
In view of the fact that most organic substances undergo rapid changes once they are deposited in geological environments, it seems likely that Scheme II will predominate over Scheme I. This being the case, it is readily seen why the origins of certain organic geochemicals are difficult to trace, and why occasionally it is necessary to use analytical techniques which, although not individually unambiguous in their results, altogether provide non-contradictory and mutually supporting evidence upon which justifiable conclusions can be based.

Classification

The many occurrences, both large and small, of organic substances having widely different physical and chemical properties have frequently prompted attempts at their classification. It would obviously simplify accurate communication among geologists, chemists, and physicists if an unknown material could be properly categorized according to a set of generally accepted criteria. It has been difficult to agree on a set of acceptable criteria, however, because organic substances of geochemical interest are subject to transformation by a number of factors. This problem can be illustrated by the fact that heat may convert one substance to a product similar to that formed from an entirely different starting substance, when the latter is metamorphosed on burial over an extended period of geological time. Thus, lignite may be up-ranked to subbituminous coal on exposure to slightly elevated temperatures for short periods, or may similarly be converted upon burial under a heavy overburden for a long period. Classification here cannot readily be made on the basis of heat, pressure, or time, but reference must be based on the original substances from which the final product was produced, or on the final product itself. By this method, the variability in metamorphic processes, although not neglected, is nevertheless eliminated from a potential classification.

Tomkeieff (1954) has attributed one of the earliest classifications of organic geochemicals to Stockar who, in 1763, arranged them essentially on the basis of their odors and viscosities. This type of classification, although empirical, has certain advantages. For one thing, the scheme is not dependent upon presuppositions with respect to the origin of a substance, and secondly, it permits comparison of any and all substances that have the same physical properties. Abraham (1945) used such a classification in comparing natural, pyrolytic, and artificial products. His scheme, shown in Fig. 3 of Chapter 8, as adapted in part by Hunt, Stewart, and Dickey (1954), is based on a combination of chemical and physical factors such as solubility in carbon disulfide, fusibility, composition, and ease of sulfonation. Obviously any asphaltic or bituminous substances, as defined by Abraham, whether they are naturally occurring or artificial, can be

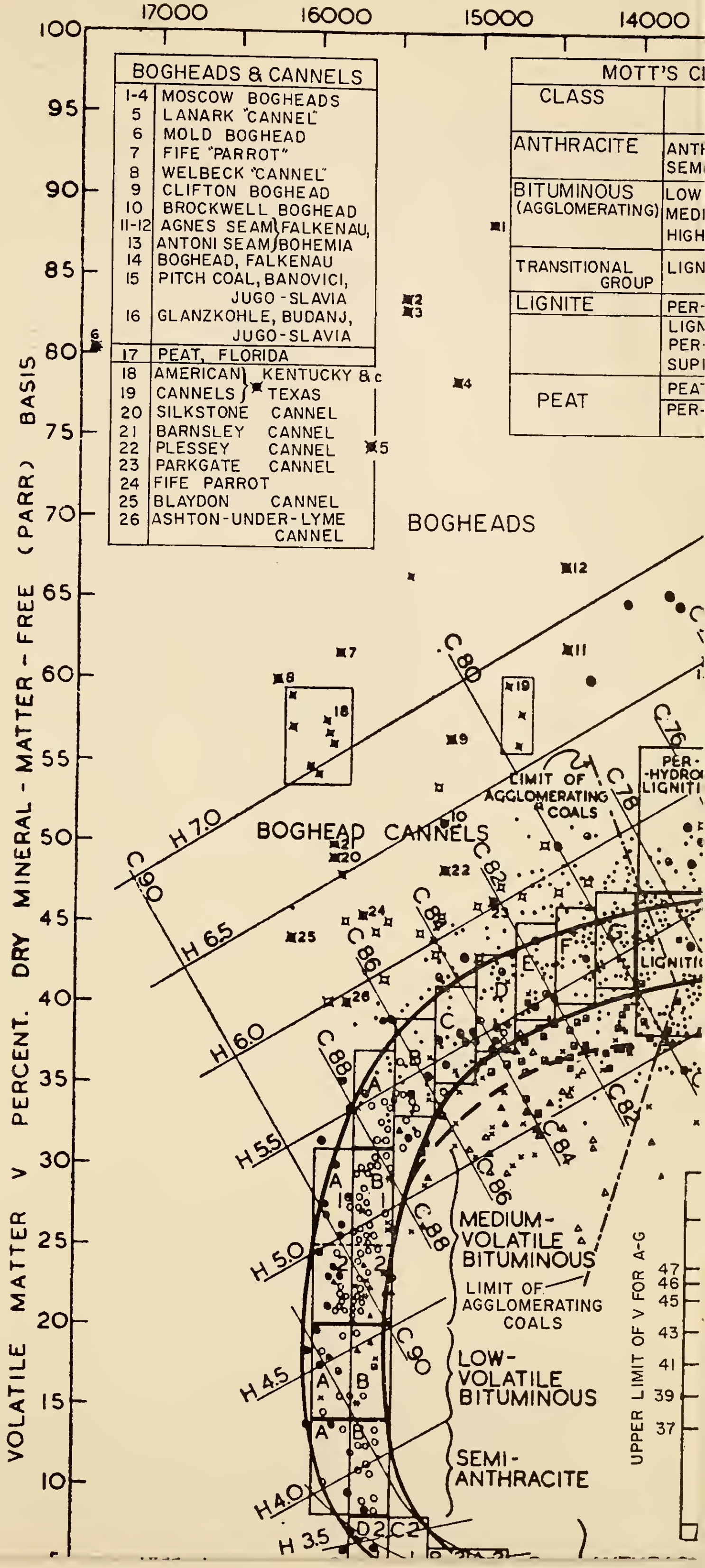

CORRECTION TO A₀ (AIR, CU.FT./lb) WHEN HYDROGEN DIFFERS FROM 54%
SCALE Y
-3·0
-2·0
-1·0
0
+1·0
+2·0
+3·0
+4·0
HYDROGEN % DRY MINERAL FREE (PARR'S BASIS)
100
8
7
6
5
4
3
Ig-Ia
FLAME
CALOR
AIR RE
WET FL
NETT C
GROSS
19%
ANTH
GR
19·5
Qg
10000
Qn
15000
V₀
150
A₀
Ig
Tᵧ
Ig-Ia
100
C

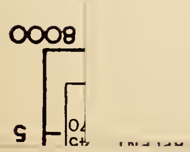


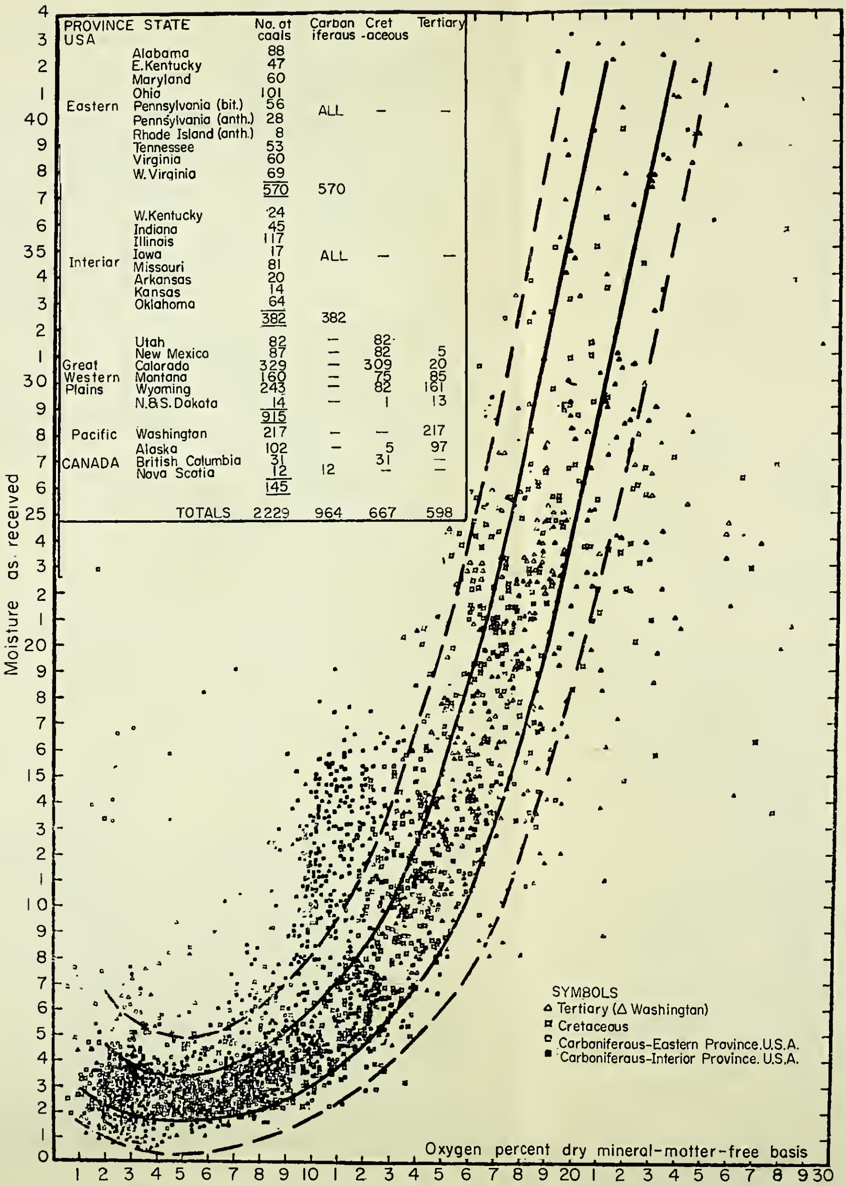
1Lb YIELDS CU.FT. (N.T.P.)		1 KILO YIELDS CU.M. (N.T.P.)	
C	29·874 OF CO_2	C	1·865 OF CO_2
H	179·241 H O (VAP)	H	11·190 H_2O (VAP.)
H_gO	19·910 " "	H_gO	1·243 " "
CO_2	8·145	CO_2	0·5085
N_2	12·803	N_2	0·7993
O_2	11·203	O_2	0·6994
AIR	12·390	AIR	0·7735

1 CALORIE/CU.M = 0·1124 B.Th U/CU.FT
1 CU.M. = 35·3148 CU.FT
1 CU.M./KILO = 16·018 CU.FT./POUND
1 CU. FT/POUND = 0·06243 CU.M./KILO

FIG. 18. Seyler's coal chart 47A.


17000
16000
15000
14000
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
VOLATILE MATTER V PERCENT. DRY MINERAL - MATTER - FREE (PARR) BASIS
BOGHEADS & CANNELS
1-4 MOSCOW BOGHEADS
5 LANARK "CANNEL"
6 MOLD BOGHEAD
7 FIFE "PARROT"
8 WELBECK "CANNEL"
9 CLIFTON BOGHEAD
10 BROCKWELL BOGHEAD
11-12 AGNES SEAM } FALKENAU,
13 ANTONI SEAM } BOHEMIA
14 BOGHEAD, FALKENAU
15 PITCH COAL, BANOVICI, JUGO-SLAVIA
16 GLANZKOHLE, BUDANJ, JUGO-SLAVIA
17 PEAT, FLORIDA
18 AMERICAN } KENTUCKY & c
19 CANNELS } TEXAS
20 SILKSTONE CANNEL
21 BARNSLEY CANNEL
22 PLESSEY CANNEL
23 PARKGATE CANNEL
24 FIFE PARROT
25 BLAYDON CANNEL
26 ASHTON-UNDER-LYME CANNEL
MOTT'S CL
CLASS
ANTHRACITE
ANTH
SEM
BITUMINOUS (AGGLOMERATING)
LOW
MEDI
HIGH
TRANSITIONAL GROUP
LIGN
LIGNITE
PER-
LIGN
PER-
SUPI
PEAT
PEAT
PER-
BOGHEADS
BOGHEAD CANNELS
LIMIT OF AGGLOMERATING COALS
PER-HYDRO LIGNITI
LIGNITI
H 7.0
H 6.5
H 6.0
H 5.5
H 5.0
H 4.5
H 4.0
H 3.5
C 90
C 88
C 86
C 84
C 82
C 80
C 78
C 76
A
B
C
D
E
F
G
D2
C2
MEDIUM-VOLATILE BITUMINOUS
LIMIT OF AGGLOMERATING COALS
LOW-VOLATILE BITUMINOUS
SEMI-ANTHRACITE
UPPER LIMIT OF V FOR A-G
47
46
45
43
41
39
37


0008
5
04
C



PROVINCE USA	STATE	No. of coals	Carboniferous	Cretaceous	Tertiary
Eastern	Alabama	88	ALL	—	—
	E.Kentucky	47			
	Maryland	60			
	Ohio	101			
	Pennsylvania (bit.)	56			
	Pennsylvania (anth.)	28			
	Rhode Island (anth.)	8			
	Tennessee	53			
	Virginia	60			
	W.Virginia	69			
		570	570		
Interior	W.Kentucky	24	ALL	—	—
	Indiana	45			
	Illinois	117			
	Iowa	17			
	Missouri	81			
	Arkansas	20			
	Kansas	14			
	Oklahoma	64			
		382	382		
Great Western Plains	Utah	82	—	82	
	New Mexico	87	—	82	5
	Colorado	329	—	309	20
	Montana	160	—	75	85
	Wyoming	243	—	82	161
	N.&S. Dakota	14	—	1	13
		915			
Pacific	Washington	217	—	—	217
	Alaska	102	—	5	97
CANADA	British Columbia	31		31	—
	Nova Scotia	12	12	—	—
		145			
	TOTALS	2229	964	667	598

FIG. 20. Mott's classification of coal showing the position of various coals in relation to the band for American coals . . . World coals . . . axes V, Q. (Mott, 1948).

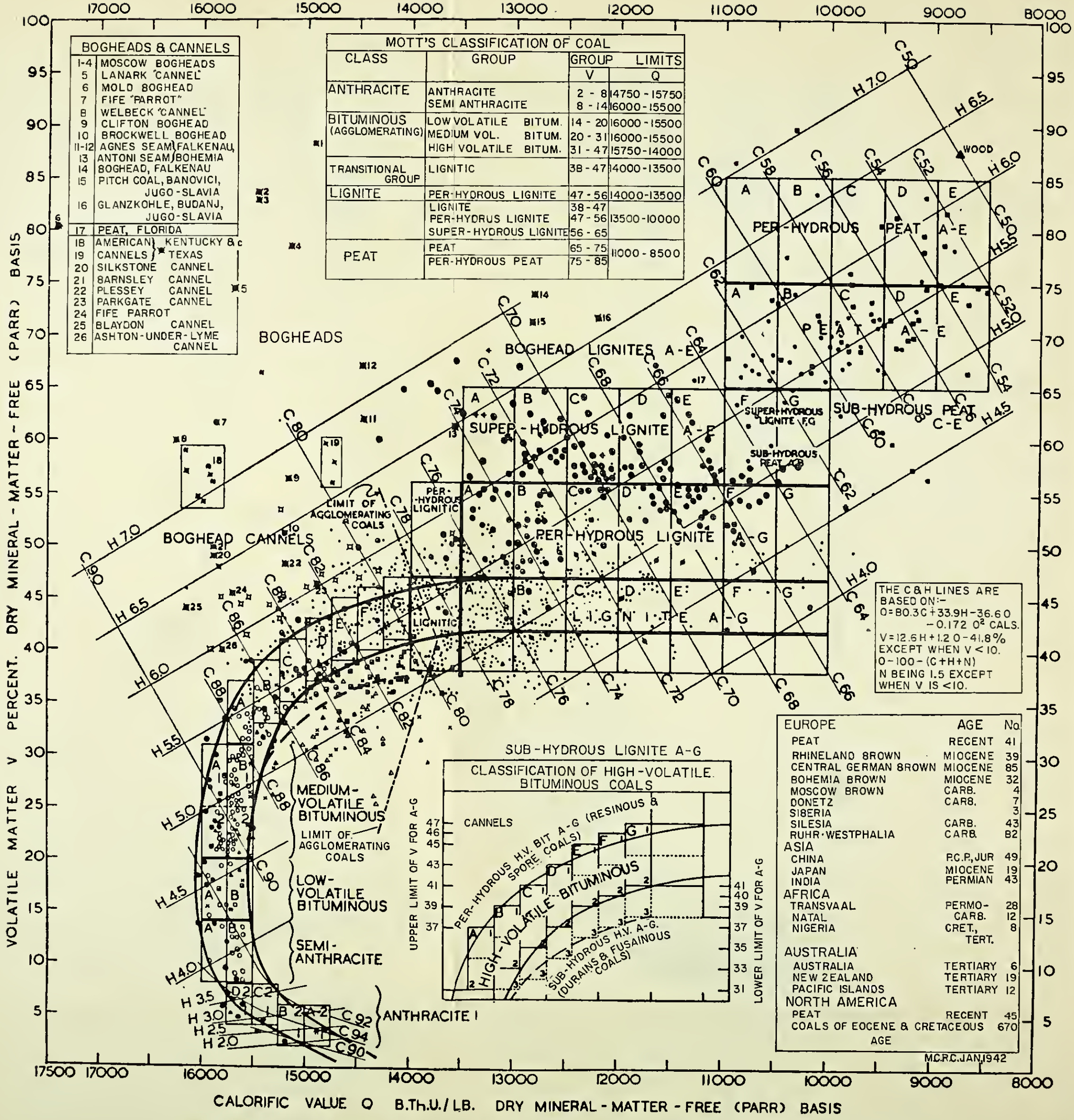
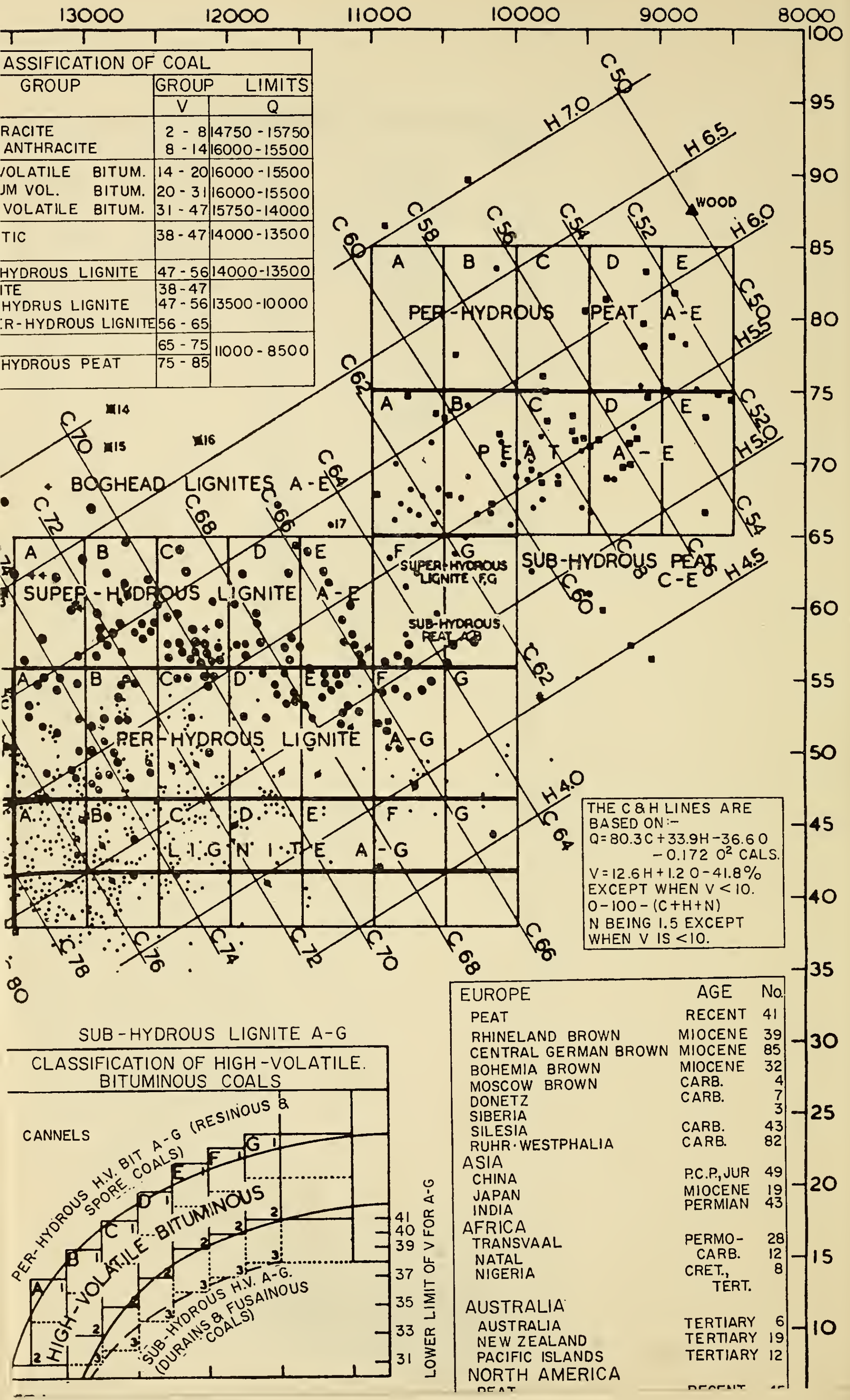


FIG. 21. Relationship between moisture, as received, and oxygen content, Parr basis, North American coals. (Mott, 1948)



ASSIFICATION OF COAL

GROUP	GROUP LIMITS V	Q
RACITE	2 - 8	14750 - 15750
ANTHRACITE	8 - 14	16000-15500
VOLATILE BITUM.	14 - 20	16000 - 15500
UM VOL. BITUM.	20 - 31	16000-15500
VOLATILE BITUM.	31 - 47	15750-14000
TIC	38 - 47	14000-13500
HYDROUS LIGNITE	47 - 56	14000-13500
ITE	38-47	13500-10000
HYDRUS LIGNITE	47 - 56	
R-HYDROUS LIGNITE	56 - 65	
	65 - 75	11000 - 8500
HYDROUS PEAT	75 - 85	

THE C & H LINES ARE BASED ON:-
$Q = 80.3C + 33.9H - 36.6O - 0.172 O^2$ CALS.
$V = 12.6H + 1.2O - 41.8\%$
EXCEPT WHEN $V < 10$.
$O - 100 - (C+H+N)$
N BEING 1.5 EXCEPT WHEN V IS <10.

CLASSIFICATION OF HIGH-VOLATILE. BITUMINOUS COALS

EUROPE	AGE	No.
PEAT	RECENT	41
RHINELAND BROWN	MIOCENE	39
CENTRAL GERMAN BROWN	MIOCENE	85
BOHEMIA BROWN	MIOCENE	32
MOSCOW BROWN	CARB.	4
DONETZ	CARB.	7
SIBERIA		3
SILESIA	CARB.	43
RUHR-WESTPHALIA	CARB.	82
ASIA		
CHINA	P.C.P., JUR	49
JAPAN	MIOCENE	19
INDIA	PERMIAN	43
AFRICA		
TRANSVAAL	PERMO-CARB.	28
NATAL		12
NIGERIA	CRET., TERT.	8
AUSTRALIA		
AUSTRALIA	TERTIARY	6
NEW ZEALAND	TERTIARY	19
PACIFIC ISLANDS	TERTIARY	12
NORTH AMERICA		
PEAT	RECENT	

classified in this scheme. In view of the absence of any alternate simple classification, that devised by Abraham has frequently been used. Unfortunately, many of the terms employed by Abraham have been used incorrectly or without redefinition by other authors thereby resulting in considerable confusion. As an example, gilsonite was recently designated in the literature as a natural asphalt, whereas Abraham specifically calls it an asphaltite.

It is not surprising that the classification of coal, which occurs in numerous forms and with highly variable properties, and which also has enormous economic importance, has received particular attention. In view of the many excellent summaries of coal classification techniques, it hardly seems necessary to review this subject in detail. Francis (1954) has discussed coal classification particularly well, and has also gone into the historical aspects of this work.

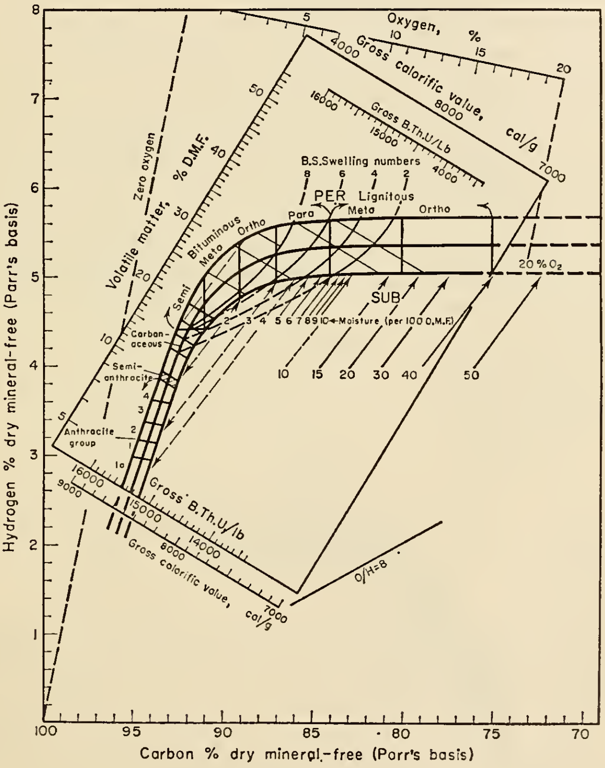


FIG. 19. Seyler's coal chart 47B.

Most classifications of coal, as far back as those of Grout (1907) and Ralston (1915), are based on ultimate analyses, in particular on carbon and hydrogen contents of the coals. The ultimate development of such classifications was eventually achieved by Seyler who, in 1948, published his Coal Charts 47A and 47B (Figs. 18 and 19) in which the carbon and hydrogen contents of coals of various rank were correlated with such other data as calorific value, free swelling index, and a host of engineering data.

Similar approaches at classification have been made by Mott, who used both proximate and ultimate analyses (1948). Mott's classification (Fig. 20) was particularly valuable inasmuch as it included a number of the rarer varieties of coal.

Many of the interrelationships noted for coal are undoubtedly the result of continuous changes in both the chemical and colloidal structure of the material. Mott's relationship between the moisture and oxygen contents of coals demonstrates this point. Here, decrease in oxygen content is related to increase in rank, which in turn is a criterion of chemical structure. Moisture retention follows this pattern linearly until the oxygen content of the coals involved diminishes beyond about 9% at which point there is an apparent change in colloidal characteristics and the moisture–oxygen relationship becomes non-linear (Fig. 21).

The continuous changes in composition and properties demonstrated by most coals have prompted many attempts at correlation for purposes of classification. With accumulation of additional data, moreover, older correlations have been re-evaluated. Thus, Essenhigh (1957) re-examined Seyler's coal curve and concluded that the data better fit the plot shown in Fig. 22 than that suggested by Seyler. Moreover, attempts have been made to establish mathematical equations by which to describe many correlations (Essenhigh, 1958), but an over-abundance of variables and complexities have made the results of such work highly controversial (Mott, 1958). The

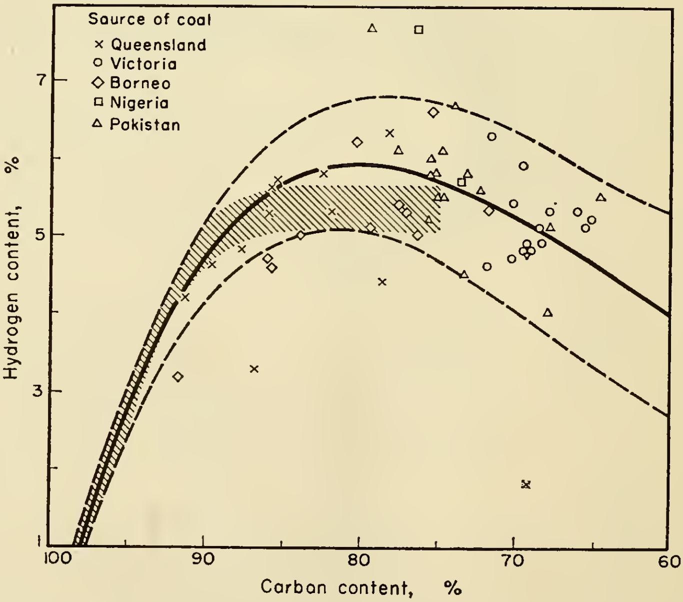


FIG. 22. Hydrogen/carbon plot of Commonwealth coals showing comparison between fitted curve and Seyler's band for bright coals (Essenhigh, 1957)

Class	Group	Limits of fixed carbon or B. t. u., mineral-matter-free basis	Requisite physical properties
I. Anthracitic	1. Meta-anthracite	Dry FC, 98 percent or more (dry VM, 2 percent or less).	Nonagglomerating.[2]
	2. Anthracite	Dry FC, 92 percent or more and less than 98 percent (dry VM, 8 percent or less and more than 2 percent).	
	3. Semianthracite	Dry FC, 86 percent or more and less than 92 percent (dry VM, 14 percent or less and more than 8 percent).	
II. Bituminous[3]	1. Low-volatile bituminous coal.	Dry FC, 78 percent or more and less than 86 percent (dry VM, 22 percent or less and more than 14 percent).	
	2. Medium-volatile bituminous coal.	Dry FC, 69 percent or more and less than 78 percent (dry VM, 31 percent or less and more than 22 percent).	
	3. High-volatile A bituminous coal.	Dry FC, less than 69 percent (dry VM, more than 31 percent); and moist[4] B. t. u., 14,000[5] or more.	
	4. High-volatile B bituminous coal.	Moist[4] B. t. u., 13,000 or more and less than 14,000.[5]	
	5. High-volatile C bituminous coal.	Moist B. t. u., 11,000 or more and less than 13,000.[5]	Either agglomerating or nonweathering.[6]
III. Subbituminous	1. Subbituminous A coal	.........ditto[5]..................	Both weathering and nonagglomerating.
	2. Subbituminous B coal	Moist B. t. u., 9,500 or more and less than 11,000.[5]	
	3. Subbituminous C coal	Moist B. t. u., 8,300 or more and less than 9,500.[5]	
IV. Lignitic	1. Lignite	Moist B. t. u., less than 8,300	Consolidated.
	2. Brown coal	.........ditto..................	Unconsolidated.

---

[1] This classification does not include a few coals that have unusual physical and chemical properties and that come within the limits of fixed carbon or B. t. u. of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free B. t. u.

[2] If agglomerating, the coal is classified in low-volatile group of bituminous class.

[3] It is recognized that there may be noncaking varieties in each group of the bituminous class.

[4] Moist B. t. u. refers to coal containing its natural bed moisture but not including visible water on the surface of the coal.

[5] Coals containing 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of B. t. u.

[6] There are three varieties of coal in the high-volatile C bituminous-coal group, namely: (1) Agglomerating and nonweathering; (2) agglomerating and weathering; (3) nonagglomerating and nonweathering.

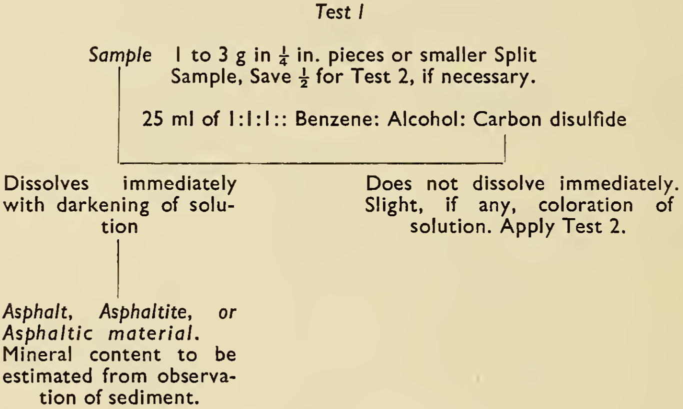
FIG. 23. Classification of coals by rank by U.S. Bureau of Mines (Fieldner and Selvig, 1957). FC, fixed carbon; VM, volatile matter; B.t.u., British thermal unit.

classifications for coal that have thus far been described are primarily based on proximate and ultimate analyses of ash- and moisture-free coal.

The U.S. Bureau of Mines uses a classification of coals by rank that is based not primarily on ultimate analyses, but, rather, on a combination of proximate values, such as fixed carbon content, and on calorific values (Fig. 23). The classification is primarily commercial and based on practice (Fieldner and Selvig, 1951), but is not particularly useful for scientific studies.

Van Krevelen (1953) tabulated similar commerical classifications as used in various countries, and in doing so clearly illustrated the variations in nomenclature that apply to the same rank of coal depending upon its country of origin.

Various classifications of coal are shown by Van Krevelen (Chapter 6), and all are essentially variations of the same theme in which bases of comparison are proximate and ultimate analyses or related physical properties.



Test I

Sample 1 to 3 g in $\frac{1}{4}$ in. pieces or smaller Split Sample, Save $\frac{1}{2}$ for Test 2, if necessary.

25 ml of 1:1:1:: Benzene: Alcohol: Carbon disulfide

Dissolves immediately with darkening of solution

Asphalt, Asphaltite, or Asphaltic material. Mineral content to be estimated from observation of sediment.

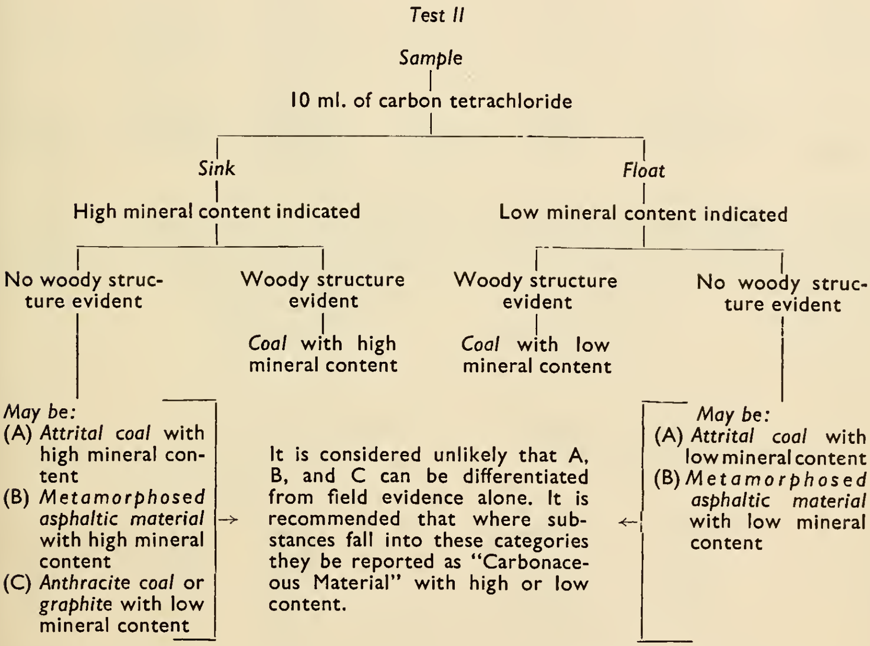
Does not dissolve immediately. Slight, if any, coloration of solution. Apply Test 2.

Note: Vein deposits such as gilsonite are soluble under the conditions of this test. If it is obvious that partial solution occurs indicating a mixture of organic substances, this should be noted. Test II can then be applied on a portion of the sample after it is washed with the solvent.

Fig. 24. Test I for field classification of naturally occurring carbonaceous substances (Deul and Breger, 1953).

Since about 1945, interest in coal hydrogenation and in the blending of coals to improve their coking properties has led to a surge of interest in the petrographic classification of coal. This work has been a direct outgrowth of the awareness that certain petrographically defined coal constituents are more amenable to hydrogenation than others, and to the fact that the petrographic constitution of coal besides its rank, governs its coking characteristics. Harrison (1961) recently reviewed problems associated with the petrographic classification of coal; the reader is also referred to work by Marshall, Harrison, Simon, and Parker (1958), and to that by Schapiro and Gray (1960). It is of particular interest that these classifications are based solely on microscopic observations. The chemical nature of the progenitor plant constituents and the degree of metamorphism, rank in the case of coal, is all indirectly taken into account.

Regularities in the metamorphic sequence of coals make their classification relatively simple. In comparison, the classification of other naturally occurring organic substances is much more difficult. In neither case is it always possible to classify an unknown material properly unless it is subjected to laboratory tests. This presents a problem for those geologists in the field who have no immediate access to laboratory facilities and yet, for various reasons, find it necessary to classify even tentatively those organic materials they may uncover. To achieve this end, Deul and Breger (1953) developed a set of simple tests to aid field geologists in characterizing and naming substances of questionable origin and properties. The tests, shown in Figs. 24 and 25, serve the purpose of simplifying the nomenclature used by those involved in reporting occurrences of organic materials. Use of improper nomenclature is minimized, thereby eliminating inferences

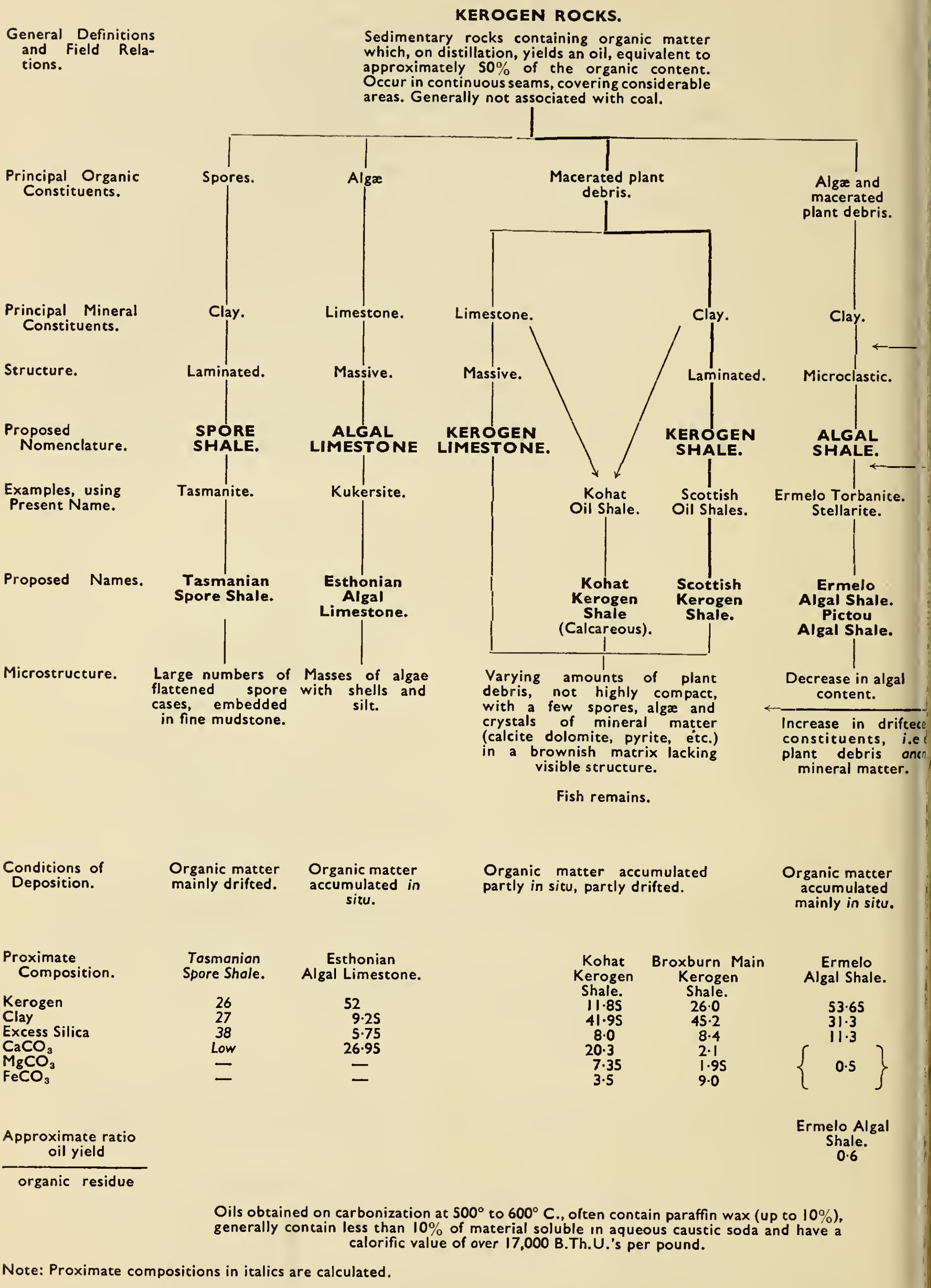

Test II
Sample
10 ml. of carbon tetrachloride
Sink
Float
High mineral content indicated
Low mineral content indicated
No woody structure evident
Woody structure evident
Woody structure evident
No woody structure evident
Coal with high mineral content
Coal with low mineral content
May be:
(A) Attrital coal with high mineral content
(B) Metamorphosed asphaltic material with high mineral content
(C) Anthracite coal or graphite with low mineral content
May be:
(A) Attrital coal with low mineral content
(B) Metamorphosed asphaltic material with low mineral content

It is considered unlikely that A, B, and C can be differentiated from field evidence alone. It is recommended that where substances fall into these categories they be reported as "Carbonaceous Material" with high or low content.

Note: Asphaltic material may be metamorphosed or altered by heat, pressure, radioactivity, or other agencies. Anthracite coal might be found in immediate proximity to a volcanic intrusion or in shear zones.

FIG. 25. Test II for field classification of naturally occurring carbonaceous substances (Deul and Breger, 1953).

that might be drawn through connotation; this problem has already been mentioned. Not only is the test scheme simple, but the terminology is consistent with that used by Abraham. As in other schemes that have already been discussed, this one presupposes no knowledge about the

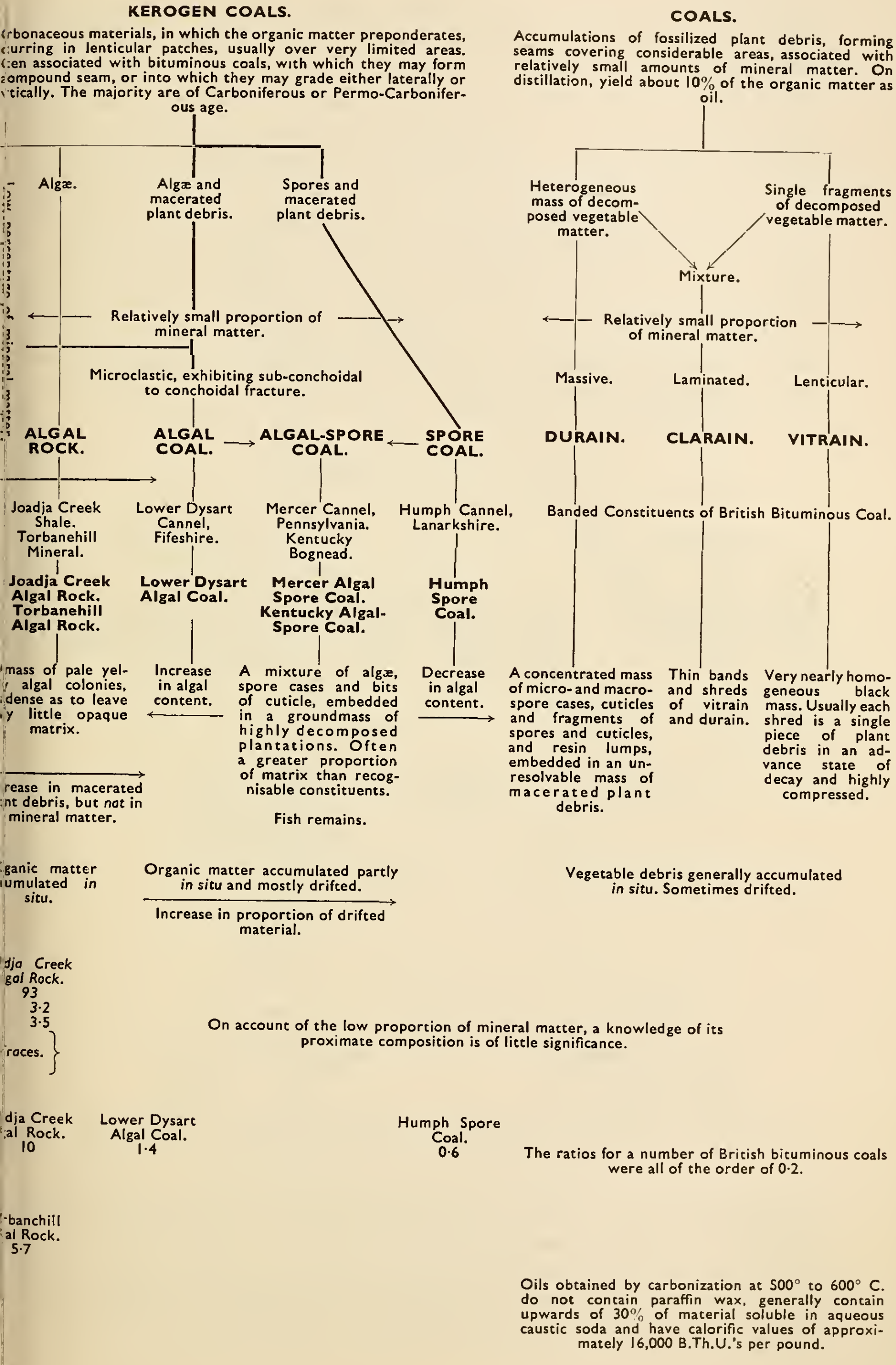


General Definitions and Field Relations.	**KEROGEN ROCKS.** Sedimentary rocks containing organic matter which, on distillation, yields an oil, equivalent to approximately 50% of the organic content. Occur in continuous seams, covering considerable areas. Generally not associated with coal.					
Principal Organic Constituents.	Spores.	Algæ	Macerated plant debris.			Algæ and macerated plant debris.
Principal Mineral Constituents.	Clay.	Limestone.	Limestone.		Clay.	Clay.
Structure.	Laminated.	Massive.	Massive.		Laminated.	Microclastic.
Proposed Nomenclature.	**SPORE SHALE.**	**ALGAL LIMESTONE**	**KEROGEN LIMESTONE.**		**KEROGEN SHALE.**	**ALGAL SHALE.**
Examples, using Present Name.	Tasmanite.	Kukersite.		Kohat Oil Shale.	Scottish Oil Shales.	Ermelo Torbanite. Stellarite.
Proposed Names.	**Tasmanian Spore Shale.**	**Esthonian Algal Limestone.**		**Kohat Kerogen Shale** (Calcareous).	**Scottish Kerogen Shale.**	**Ermelo Algal Shale.** **Pictou Algal Shale.**
Microstructure.	Large numbers of flattened spore cases, embedded in fine mudstone.	Masses of algae with shells and silt.	Varying amounts of plant debris, not highly compact, with a few spores, algæ and crystals of mineral matter (calcite dolomite, pyrite, etc.) in a brownish matrix lacking visible structure. Fish remains.			Decrease in algal content. Increase in drifte constituents, *i.e* plant debris *an* mineral matter.
Conditions of Deposition.	Organic matter mainly drifted.	Organic matter accumulated *in situ*.	Organic matter accumulated partly *in situ*, partly drifted.			Organic matter accumulated mainly *in situ*.
Proximate Composition.	*Tasmanian Spore Shale.*	Esthonian Algal Limestone.		Kohat Kerogen Shale.	Broxburn Main Kerogen Shale.	Ermelo Algal Shale.
Kerogen	*26*	52		11·85	26·0	53·65
Clay	*27*	9·25		41·95	45·2	31·3
Excess Silica	*38*	5·75		8·0	8·4	11·3
$CaCO_3$	*Low*	26·95		20·3	2·1	0·5
$MgCO_3$	—	—		7·35	1·95	
$FeCO_3$	—	—		3·5	9·0	
Approximate ratio $\frac{\text{oil yield}}{\text{organic residue}}$						Ermelo Algal Shale. 0·6

Oils obtained on carbonization at 500° to 600° C., often contain paraffin wax (up to 10%), generally contain less than 10% of material soluble in aqueous caustic soda and have a calorific value of *over* 17,000 B.Th.U.'s per pound.

Note: Proximate compositions in italics are calculated.

FIG. 26. The classification of kerogen rocks and kerogen coals showing their interrelationships and their gradation into bituminous coals (Down and Himus, 1940).



KEROGEN COALS.

(rbonaceous materials, in which the organic matter preponderates, (:urring in lenticular patches, usually over very limited areas. (:en associated with bituminous coals, with which they may form compound seam, or into which they may grade either laterally or \ticaliy. The majority are of Carboniferous or Permo-Carboniferous age.

Algæ.

Algæ and macerated plant debris.

Spores and macerated plant debris.

Relatively small proportion of mineral matter.

Microclastic, exhibiting sub-conchoidal to conchoidal fracture.

ALGAL ROCK. **ALGAL COAL.** → **ALGAL-SPORE COAL.** ← **SPORE COAL.**

Joadja Creek Shale. Torbanehill Mineral.

Joadja Creek Algal Rock. Torbanehill Algal Rock.

mass of pale yel- algal colonies, dense as to leave y little opaque matrix.

rease in macerated nt debris, but *not* in mineral matter.

Lower Dysart Cannel, Fifeshire.

Lower Dysart Algal Coal.

Increase in algal content.

Mercer Cannel, Pennsylvania. Kentucky Bognead.

Mercer Algal Spore Coal. Kentucky Algal-Spore Coal.

A mixture of algæ, spore cases and bits of cuticle, embedded in a groundmass of highly decomposed plantations. Often a greater proportion of matrix than recognisable constituents.

Fish remains.

Humph Cannel, Lanarkshire.

Humph Spore Coal.

Decrease in algal content.

ganic matter umulated *in* situ.

Organic matter accumulated partly *in situ* and mostly drifted.

Increase in proportion of drifted material.

COALS.

Accumulations of fossilized plant debris, forming seams covering considerable areas, associated with relatively small amounts of mineral matter. On distillation, yield about 10% of the organic matter as oil.

Heterogeneous mass of decomposed vegetable matter.

Single fragments of decomposed vegetable matter.

Mixture.

Relatively small proportion of mineral matter.

Massive. Laminated. Lenticular.

DURAIN. **CLARAIN.** **VITRAIN.**

Banded Constituents of British Bituminous Coal.

A concentrated mass of micro- and macro-spore cases, cuticles and fragments of spores and cuticles, and resin lumps, embedded in an unresolvable mass of macerated plant debris.

Thin bands and shreds of vitrain and durain.

Very nearly homogeneous black mass. Usually each shred is a single piece of plant debris in an advance state of decay and highly compressed.

Vegetable debris generally accumulated *in situ*. Sometimes drifted.

dja Creek gal Rock.
93
3·2
3·5
races. }

On account of the low proportion of mineral matter, a knowledge of its proximate composition is of little significance.

dja Creek al Rock. 10

Lower Dysart Algal Coal. 1·4

Humph Spore Coal. 0·6

The ratios for a number of British bituminous coals were all of the order of 0·2.

-banchill al Rock. 5·7

Oils obtained by carbonization at 500° to 600° C. do not contain paraffin wax, generally contain upwards of 30% of material soluble in aqueous caustic soda and have calorific values of approximately 16,000 B.Th.U.'s per pound.

origin of certain organic substances. Also, the elimination of potentially confusing names prevents misconceptions that may arise with respect to the nature of the materials.

An extremely useful classification of shales and coals was published by Down and Himus in 1940. The arrangement of substances (Fig. 26) was developed by these authors as a result of the need for a standard nomenclature of naturally occurring substances that yield oil on distillation. In essence, the systematization is based upon knowledge of the principal organic constituents, of the principal minerals, and of the conditions under which the substances were deposited. As shown, many names had previously been applied to closely related substances leading to confusion. Of particular importance is the very useful designation of major mineral constituents, for the origin and fate of organic matter probably both differ depending upon whether the material is deposited in a limestone or clay environment.

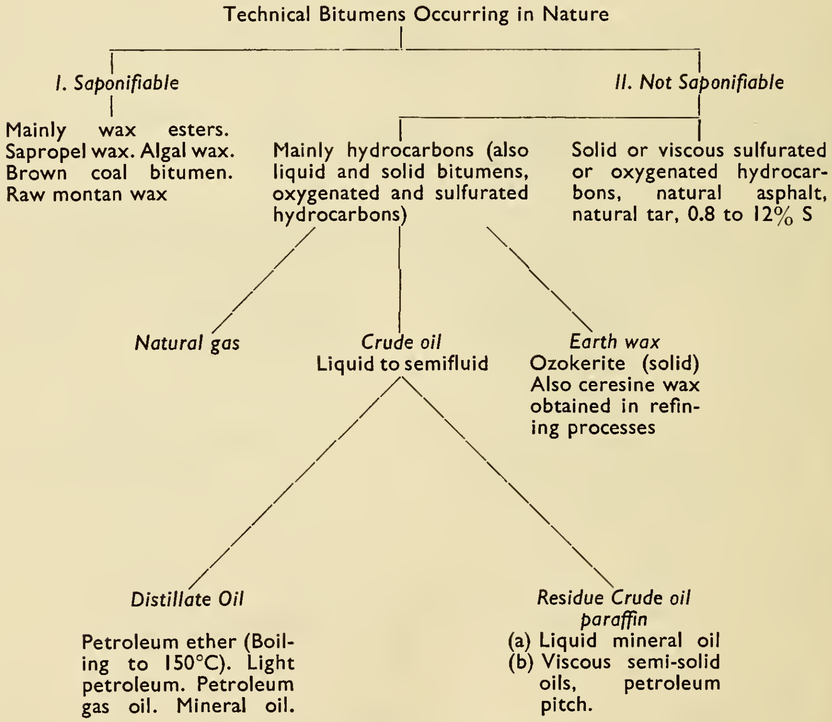

Technical Bitumens Occurring in Nature
I. Saponifiable
II. Not Saponifiable
Mainly wax esters. Sapropel wax. Algal wax. Brown coal bitumen. Raw montan wax
Mainly hydrocarbons (also liquid and solid bitumens, oxygenated and sulfurated hydrocarbons)
Solid or viscous sulfurated or oxygenated hydrocarbons, natural asphalt, natural tar, 0.8 to 12% S
Natural gas
Crude oil
Liquid to semifluid
Earth wax
Ozokerite (solid)
Also ceresine wax obtained in refining processes
Distillate Oil
Petroleum ether (Boiling to 150°C). Light petroleum. Petroleum gas oil. Mineral oil.
Residue Crude oil paraffin
(a) Liquid mineral oil
(b) Viscous semi-solid oils, petroleum pitch.

FIG. 27. Classification of natural bitumens by Gothan (1949).

Although the Down–Himus classification is useful for the categorization of shales and coals, no attempt is made in it for classification of other naturally occurring organic substances such as crude oil, waxes, gas, etc. Gothan (1949) categorized such substances on the basis of their chemical structure as defined by whether or not they are saponifiable.

Gothan's classification (Fig. 27) is in many respects not unlike that of Abraham, the prime difference being the chemical basis of comparison. Inasmuch as the chemical structures of these substances govern their physical properties, the two classifications take on many similarities.

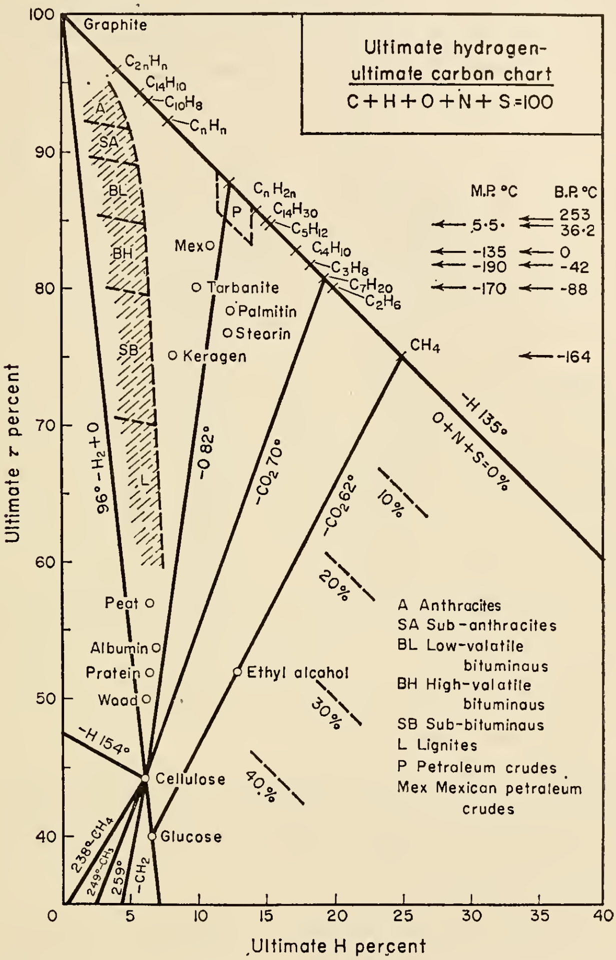


FIG. 28. Owen's classification of carbonaceous substances (1948).

Paclt, in 1953, attempted a more complete organization and tabulation of naturally occurring organic substances than that proposed by Gothan. Paclt's paper is particularly useful for its extensive list of names that have been used for organic geochemicals or, as they have been called by Potonie (1908) "caustobiolites", and by Paclt, "caustolites". Over 250 such names are tabulated and arranged in three broad classes based upon physical condition and descriptive mineralogy or petrology. Unfortunately, the chemical criterion used as one of the three bases for the classification is inordinately broad, its divisions being purely into inorganic and organic sub-classes. Moreover, Paclt's development of new class names offers little help for an already confused nomenclature.

The classifications that have been described are primarily based upon the properties of the compounds that are being compared. A number of somewhat more fundamental approaches have been developed, however, in which chemical compositions of the organic geochemicals have been plotted in diagrams designed to illustrate regularities in chemical reactions that may occur during the diagenesis of the progenitors to form the ultimate products. Such graphical representations, as that by Owen (1948) shown in Fig. 28, are primarily based on ultimate analyses.

As illustrated, the diagram is not unlike that previously shown for the classification of coals. Here, too, a triangular plot, in which the apices of the diagram are percent carbon, percent hydrogen, and percent total oxygen, nitrogen, and sulfur, has been reconstructed to a rectangular form. Owen chose cellulose, because of its ubiquity, as a starting point for his considerations and drew lines through the composition of cellulose until they intersected the zero percent $(O+N+S)$ line at various hydrocarbon compositions. Thus removal of carbon dioxide (decarboxylation) from cellulose along a path having a slope of 70° will ultimately lead to hydrocarbons having the total composition C_7H_{20}, which could be equivalent to a mixture of 2 moles of ethane (C_2H_6) and one mole of propane (C_3H_8). Decarboxylation is neither oxidation nor reduction, but resembles fermentation; the same analysis applied to glucose as the starting material yields, with a line having a 62° slope, ethyl alcohol and eventually methane.

By Owen's technique, it is possible to conceive of reactions such as decarboxylation, deoxygenation, dehydrogenation, or demethanation as being of particular importance in the diagenesis of natural substances. Needless to say, this approach can be of extreme value in the correlation of organic geochemicals, both in aiding in an understanding of possible progenitors and in the diagenetic changes they have undergone. Also, it is possible in this type of classification to correlate interrelationships between substances with widely divergent histories.

Several other classifications not unlike that of Owen have also been suggested. Grigor'ev (1954) constructed a diagram also based on cellulose in which water and carbon are eliminated (Fig. 29), and van Krevelen's atomic H/C *vs.* O/C diagram (Chapter 6) is extremely useful for following chemical changes in coals and other substances.

All classifications that have been developed to date have great utility but must be used with care. In dealing with organic geochemicals it is necessary to emphasize again that the variables in any problem may be manifold. Proper solution of a characterization problem requires information as to the geological setting in which the substance in question occurs, information as to its physical and chemical properties, observations on its mineral constituents, data on its chemical structure such as may be obtained by infrared analysis and, finally, the use of a classification diagram such as that of Owen, Grigor'ev, or van Krevelen. Complete and unambiguous solutions to problems associated with the origin and metamorphism of such substances are rarely simple to obtain, and invariably one must be content with a situation in which all the analytical information points in a particular direction. It should be firmly kept in mind that classification schemes, useful as they may be, are usable only in conjunction with and as an auxiliary to a great deal of fundamental information.

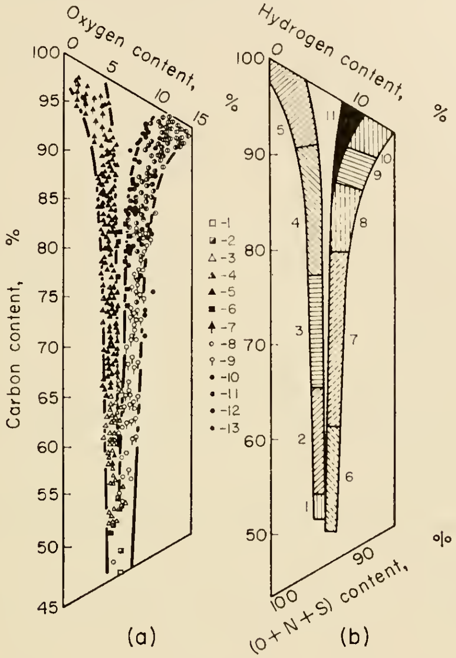


FIG. 29. Classification diagram of A. S. Dobryansky as cited by Grigor'ev (1944)
(a) 1. Cellulose; 2. wood; 3. peat; 4. brown coal; 5. subbituminous coal; 6. bituminous coal; 7. anthracite; 8. algal material; 9. shale; 10. sapropelite; 11. asphalt; 12. asphalt; 13. petroleum.
(b) 1. Wood; 2. peat; 3. brown coal; 4. subbituminous coal; 5. anthracite; 6. algal material; 7 shales; 8. sapropelite; 9. asphalt; 10. petroleum; 11. asphalt.

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Chapter 4

GEOCHEMISTRY OF HUMUS*

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Definition and Nature

Definition—Humus includes all the dark colored organic constituents found in "soil" or other sedimentary accumulations (Fraser, 1955). The term, as further defined, includes certain uncolored or light colored organic substances such as waxes, resins, and hydrocarbons associated with or the product of organic decomposition. Humus is viewed as the product of activity of soil microflora, rather than the result of simple chemical transformation of the starches, proteins, etc., of plants (Geltser, 1940).

With reference to humus in soils, the following constituents may be included: (1) Plant residues in various stages of decay; (2) decay products of plants and animals; (3) coprogenic products of animals in or on the soil; and (4) associated live organisms. The same association of materials would be found in lacustrine or marine as well as in terrestrial humus. Humus forms in modern "dust bowls" where cultivation has exposed large areas rich in soil organic matter to the mercy of the winds, and this *atmospheric* humus may be spread widely. In certain industrial and urban areas, humus is a constituent of "smog".

In the soil, a deposit (*mull*) of humus mixed with considerable inorganic matter may be formed by the mixing action of worms and smaller organisms. In forest or meadow litter, layers of partly decomposed, comminuted "raw humus" are underlain by fully decomposed humus or *mor* (Fraser, 1955).

Upland or moor accumulations of *Sphagnum* and other moss may decompose to form a humus of *highmoor peat* (Waksman, 1936). Lowland bog or muskeg accumulations of moss, swamp, and forest vegetation produce *lowmoor peat* of denser texture, higher moisture content, and less acidity than highmoor peat. An amorphous, gummy concentration of humic substance beneath or within some peat bogs has been termed *dopplerite*.

In eutrophic lakes and in marshes the gathering of settled plankton, pondweeds and associated bacteria, animals and mineral matter forms a brown or gray pulpy coprogenic substance, lake peat, ävja-gyttja (Naumann, 1929) or *copropel* (Swain and Prokopovich, 1954). Black, mainly anaerobic masses of humus in deeper hypolimnetic areas of lakes and bays or among pondweeds or salt marshes, particularly in high sulfate waters, is *sapropel* (Wasmund, 1930). The pondweed type of sapropel is believed to originate from cellulose-rich higher plants and is termed *förna* (Lindeman, 1941b).

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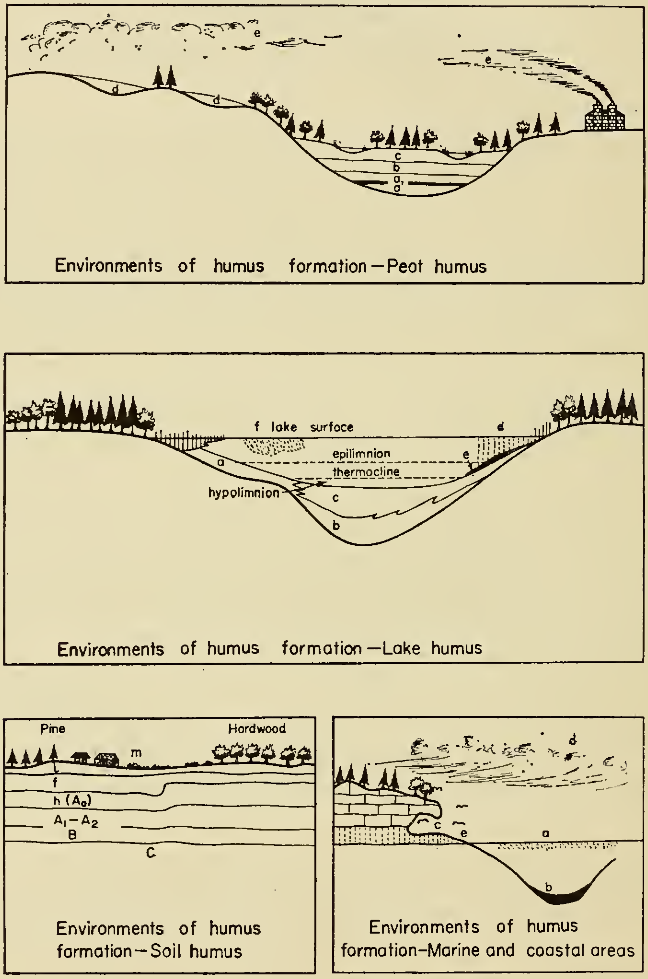
* Submitted in 1958.

Deposition on floors of brown-water or dystrophic lakes comprises an allochthonous precipitate of humic acids and detritus known as *dy* (Lindeman, 1941b).



Environments of humus formation—Peat humus

Environments of humus formation—Lake humus

Environments of humus formation—Soil humus

Environments of humus formation—Marine and coastal areas

FIG. 1. Sketches to show various situations in which humus forms.

Marine, presumably proteinaceous, slime resulting from settled planktonic detritus has been called *pelogloea* (Fox, Issacs, and Corcoran, 1952) and is evidently comparable to copropel of lakes. Various natural situations in which humus may form are shown in Fig. 1.

Determination and preparation of humus—Because of the complexity of humus, attempts to separate its constituents have been mainly confined to recognition of "operational units". A typical procedure is as follows:

The soil is extracted with sodium hydroxide to yield soluble *humus* and to leave behind insoluble unhumified plant residues and *humin*. The humus solution is acidified with excess hydrochloric acid to yield a brown or gray *humic acid* precipitate; *fulvic acid* remains in solution. The dried humic acid is treated with alcohol to separate a fraction termed *hymatomelanic acid*.

Humus has been determined by the following method (Nostilz, 1936): the humic sample (0.2 to 1 g) is added to a mixture of 30% sulfuric acid (20 ml.), 0.1 N potassium permanganate (2 ml/mg of carbon expected) and water to make the concentration of the $KMnO_4$ 0.025 N. After boiling, a measured excess of 0.1 N acetic acid is added and back-titrated with 0.1 N $KMnO_4$. Each ml of 0.1 N $KMnO_4$ consumed is equivalent to 0.51 mg carbon as determined comparatively by combustion analysis. The dry humus is determined by $C \times 1.72$. Experimental evidence shows that hydrous ferric oxide and manganese dioxide have little or no effect on the result, and fresh vegetation is resistant to the permanganate. Peat and marl give unreliable results.

Several different methods of humus determination in the 1930's and 1940's have been discussed and evaluated (Bajdalakov, 1934; Meurice and Martens, 1934; Crowther, 1935; Sibirshii, 1935; Tyurin, 1935; Puri and Sarup, 1937; Gollan and Mallea, 1940; Thieme, 1937; Springer, 1937; Waksman, 1938) with the conclusion that, in that period of investigation, extraction with $KMnO_4$ produced the most reliable results. More recent work (Fraser, 1955) has shown pyrophosphate to be preferable to alkaline extraction when fractionation of the humus is to be carried out, because alkalis alter the humus.

A study of the determination of the humus content of soil by extraction with ammonia (Meurice and Martens, 1934) shows the resulting values to be high because clay minerals containing moisture go into suspension in the ammoniacal liquid and on ignition lose their moisture, which is calculated as organic matter. Flocculation of the suspension with $(NH_4)_2CO_3$ helps to eliminate this error.

When samples of soil containing humus were extracted with NaOH or Na_2CO_3, the extracts were colored; samples containing only fresh vegetable matter yielded uncolored extracts (Thieme, 1937). The effect of adding sodium chloride to peat and brown coal before treatment with sodium hydroxide is to increase the yield of alkali humates (Natansou, 1956).

A method of separating "gray humus" from "brown humus" involves boiling the sample in 5% sodium hydroxide for one hour, followed by centrifuging and washing with 2% sodium hydroxide thus removing brown humus. The residue is extracted 48 hours with acetyl bromide and ignited, and the humus charcoal plus "gray humus" are thus determined. If a second sample be treated with warm water in place of acetyl bromide, water soluble gray humus may be determined (Springer, 1937).

Artificial preparation of "humus" by HCl-extraction of cane sugar has been described by Tokuoka and Dyo (1938). The formation of humus-like substance is said to result from rye and wheat grains kept for a long time in a moist condition at temperatures of 30–40°C.

A procedure for the testing of peat with respect to its medicinal uses (balneology) has been described and includes methods for determination of bitumens, pectins, carbohydrates, etc. (Souci and Quentin, 1954).

Classification—Attempts have been made to subdivide humus and classify it on both a physical and a chemical basis. Fractionation of soil organic matter to produce operational categories such as humus, humin, fulvic acid, humic acid and hymatomelanic acid was described above. Preliminary treatment of the humic sample with solutions of acetyl bromide or acetic anhydride-sulfuric acid is said to remove the non-humidified organic matter.

Important strides have been made in the characterization of substances present in these isolates; some of the results are given below (Fraser, 1955, p. 164):

(1) Humin fractions extracted with acetyl bromide: polymerization products of humic and fulvic fractions, plus plant and microbial tissues.

(2) Fulvic acid fraction: pentosans and uronic acid, which are constituents of uronide hemicelluloses; polyuronide complexes; phenolic glucosides; sugars; and amino acids.

(3) Humic acid fraction.

  (*a*) hydrolyzable part: sugars and proteins.

  (*b*) Unhydrolyzable part, possibly derived from lignin, the following organic groups: phenolic (ArOH), carboxyl (—COOH) more than in lignin, acetyl (RCO—), methoxyl (CH_3O—) less than in lignin, and hydroxyquinone (as $C_6H_2O_2(OH)_2$), the latter possibly responsible for the darkening of some peats on exposure to air; nitrogen, probably bound to the ligniferous molecules.

Subdivision of soil humus into two main types was recognized by Springer (1934): I. *Cassel brown* type found in acid soils or in little-humified alkaline or neutral soils, soluble in NaOH at any concentration, rather easily decomposed and leaches readily from soil; II. *Black earth* type, present chiefly in black soils, in purest form in humus silicate complexes, formed in strongly humified soils, is more sensitive than I. to precipitation by electrolytes, particularly excess alkali, formed by anaerobic organisms.

One of the early attempts at humus classification was by Julien (1880) who recognized: (1) brown humus occurring in living vegetation, new forest litter, peat, decomposing sea weeds of the intertidal zone and in fungi; (2) black humus of deeper layers of soil, decomposing leaves and wood of forest, animal manures, peat of swamps, and in muds; (3) humus in a state of transference occurring in river, lake, spring, and rain water; (4) humus of lignite, carbonaceous rocks, and in such minerals as iron and manganese hydroxides.

A classification of humus based upon genesis was developed by Waksman (1938, p. 8) and is summarized as follows:

(A) Humus types formed by decomposition of plant and animal residues under aerobic or only partly anaerobic conditions, in composts and in soil:

- I. Humus of composts (with 3 subdivisions).
- II. Humus in soil.
  - (1) Plant residues decomposed under conditions of high acidity or low temperature or both (with 3 subdivisions).
  - (2) Plant residues decomposed under less acid, neutral or alkaline conditions: typical soil humus.
- III. Air-borne or atmospheric humus (added here).

(B) Humus types formed by decomposition of plant and animal residues under anaerobic conditions:

- I. Recent formations:
  - (1) Highmoor peats
  - (2) Lowmoor peats
  - (3) Forest and transition peats
  - (4) Sedimentary peats
- II. Old formations:
  - (1) Soft coals
  - (2) Hard coals

(C) Humus types formed in water basins:

- I. Recent formations:
  - (1) Water-soluble humus
  - (2) Humus in marine bottoms
  - (3) Humus in sewage sludge
- II. Geologic formations:
  - (1) Source beds of petroleum.

Physico-Chemical Properties and Reactions

Generalized chemical nature—The generalized chemical nature of various kinds of humus was discussed by Waksman (1938). The humic components of decomposed plant remains comprise a varying proportion of lignin or lignin derivatives and protein, together with a less stable group of resistant carbohydrates and fatty and waxy substances. Lowmoor or swamp peats are nearly 70% ligno-protein as compared with 36% in the original plants; highmoor or moss peats have corresponding values of 36% and 13%, respectively. Chernozem soil contains calcium and magnesium with its humus in the form of humates and as carbonates. Narrow carbon: nitrogen ratios of about 10 : 1 are characteristic of chernozem soils, and their humus is fixed owing to the abundant bases (Flieg, 1935). Soils of acid regions tend to be high in protein and to have narrow carbon : nitrogen ratios. In chestnut soils the humus is intermediate chemically between that of chernozems and that of serozems.

Oxidation of humus is retarded by the presence of alkalis and this retarding action is in the order H < Na < Ca.

An attempt to follow the titration of "humic acid" by Na_2CO_3 in diethylene glycol by determining viscosity, color or changes in condition gave divergent results for the number of carboxyl groups in various examples of humic acid. The results provide a further indication of the complex physico-chemical makeup of "humic acids".

Effect of humus on Hydrogen-ion concentration—The water soluble percolates of raw A_1-horizon Quebec humus showed pH values ranging from 3.8 to 5.4 (Atkinson and McKibbin, 1934). The concentrates of this material could be fractionated by dialysis through Cellophane, and the percolates of five soils proved to have up to 23% of the total acidity H_2SO_4. In one sample P_2O_5 accounted for 28% of the total acidity. The importance of these common and widespread acids is generally overlooked in geological textbooks.

Antiseptic properties—Removal of humus from cellulose hydrolyzates was accomplished by treatment with dilute aqueous solution of ClO_2 (Waksman, 1938). It was found that accurate determination of the hexoses by bacterial fermentation was hampered by the fermentation-restraining humic substances, further evidence of the antiseptic nature of humus that had been emphasized by others. The presence of phenols, quinones, phenol carboxylic acids and phenol glucosides in peat deposits has been cited (Rakovskii, 1953). These materials are believed to act as antiseptics to retard the activity of microorganisms.

The relationship between pH ,Eh, and possible antiseptic properties of peat was discussed by Swain and Prokopovich (1954). The nearly neutral pH and the slightly oxidizing redox potentials in the peats of Cedar Creek Bog, Minnesota, are believed to be the result of the disseminated humic substances that are shown by infrared absorption spectra to contain phenolic compounds (Swain, 1956). Samples of peat and lake sediments from Minnesota, stored in their own water, have remained unchanged for as long as eight years.

Striking examples of the preservative nature of peat water are the human remains of "lake people" about 2000 years old that have been recovered in an excellent state of mummification from peat bogs in Denmark (Glob, 1951); see also Chapter 12.

Effect on solubility of transported inorganic ions—Humus in the form of alkali humates from lignite was found to impede precipitation of PO_4^{3-} by Ca^{2+} over the pH range 4.2–8.0 (Apushkin, 1935). Pure $Ca_3(PO_4)_2$, apatite, and other phosphates are dissolved by the humus solution at pH 7.8. The resulting solution allows P_2O_5 to percolate easily through soil. Geologically this may be important in the concentration of phosphate minerals such as vivianite and bobierrite in the lower parts of peat bogs. Phosphorus may also be leached from iron or aluminum phosphates by the action of humic acids (Noda and Saio, 1954).

Other aspects of this subject are discussed under "Properties of adsorption in humus" and "Mineral concentrations related to humic materials".

Physical properties—The physical and physico-chemical properties of humus as they were understood through 1938 were thoroughly reviewed by Waksman (1938, p. 308–331); only factors of geological significance are discussed here. The following properties were considered by Waksman: (1) color, (2) characteristic structure, (3) volume weight, (4) properties of cohesion and adhesion, (5) specific weight, (6) high water-holding capacity, (7) high permeability, (8) heat capacity and heat absorption, (9) shrinkage on drying, (10) coagulation by electrolytes, (11) absorption of salts and gases (high base exchange capacity), (12) high buffering power, and (13) specific odor.

Although depth of color due to humus has been used for soil classification, it is unreliable as an indicator of humus content owing to degree of decomposition, presence of iron sulfide, etc. The dark color of alkaline extracts of humus is not necessarily caused by oxygen absorption during the extraction nor does it *per se* indicate the presence of phenolic compounds (Shorey, 1930).

The sedimentary structure of humus is governed by the original fabric of the source material, and its diagenetic history. The structure of forest peat is so vastly different from lake peat (copropel) that almost no physical properties are common to the two.

The loss of cohesion of peat and copropel on freezing is very striking. In general, humus has lower cohesion than clay, but silt-free dry copropel has very high cohesion.

The water-holding capacity of pure fresh humus of all kinds is high, 85–89% or more. As the mineral content increases, the water content of fresh humus decreases (Swain, 1956, p. 630). Once dry, most humus is not easily wetted again by water owing to absorbed air bubbles, although freezing may restore the wettability. "Liver peat" is said to retain its wettability after drying.

Study of the moisture content of peat from Cedar Creek Bog, Minnesota (Swain and Prokopovich, 1954) gave the following results: forest peat 88–89%, sedge peat 91–94%, copropel (gyttja) 90–93%, sapropel 87–90%, marl 56–79%. The lower moisture content of the marl may result partly from compaction, but this substance apparantly does not ever attain the high moisture content of peat and copropel unless mixed with large quantities of the latter material. Moisture contents of organic lake deposits in Minnesota were studied by Swain (1956) and the following averages were observed: lake peat, 75–90%, with the coarser pondweed peats having the lower values; copropel $> 85\%$ but the degree of siltiness, which reduces moisture content, is so variable that average figures are difficult to determine; and marl 35–43% depending on quantities of silt, sand and copropel.

The shrinkage of copropel, 80% or more, is very great, on drying. Peat, marl, and sand show far less shrinkage because they have less water initially and they retain more pore space after drying (Swain, 1956).

Colloidal properties—A series of investigations have been made which are related to the colloid-forming properties of humus (Waksman, 1938, p. 312–15). Association of humus colloids with clay colloids protects the humus from decomposition.

The colloidal nature of humus was recognized by van Bemmelen, and experiments in the electrodialysis of humus have shown it to be separable into several fractions. "Humic acid" can be concentrated and purified by electrophoresis; it apparently consists of particles about $0.02\ \mu$ in diameter which migrate with a negative charge in the electrical field.

The bonding relationships between humus and mineral colloids is postulated as a function of three types of humus (Tyulin, 1938): first, calcium and magnesium humates separated by Gedroiz's hydrogen peroxide method; second, humates released by treating the residue from the first process with weak acid and alkali; third, humates in which the exchange capacity is unaffected by treatment with H_2O_2 or which remain bonded to mineral colloids after treatment with fairly strong acids, strong alkali or by boiling with pyridine.

It is believed by some workers that the acidic properties of humus colloids result from surface or adsorption phenomena because of their low electrical conductivity and their degree of absorption of salts (Waksman, 1938, p. 314). Others, however, believe that true organic acids provide the acid nature of humus; both may be true in certain cases.

When osmotic pressure measurements were made on amylophosphoric acid obtained from ammonium humate, hymatomelanate and other sources (Samec, Knop and Pankovič, 1932), osmotic inactivity of ions of opposite charge was found.

The colloidal properties of a chernozem were studied by Aleshin and Boleritskaya (1940) who found the following relationship of coagulating agencies on a humus solution: $Na^+ < Ca^{2+} < H^+ < Al^{3+}$. Intensive Brownian movement of the particles in solution was observed. When an oxalate solution of humus was subjected to electrophoresis, the humus particles moved in the direction of the positive pole. The facts were taken to indicate that humus oxalates are hydrophobic colloids.

The adsorption isotherms of $Ba(OH)_2$ by humic acids and by fusite were studied (Syskov, 1936) and it was found that the Ostwald and Van't Hoff equations did not give constant values of K (equilibrium constant). Adsorption of the $Ba(OH)_2$ was followed by chemical reaction with the humic acids. Similar reactions with minerals may have geological importance in the movement of humic substances in the sediments.

The viscosity of humic colloids was found to be affected by the presence of various electrolytes in the following order (Boutaric and Thévenet, 1937): NaOH, KCl, NaCl, $BaCl_2$, HCl, $AlCl_3$. The study indicated that humic colloids are intermediate between hydrophilic colloids and suspensoids. Most humic colloids apparently consist of micelles that have little or no effect on surface tension. An attempt was made to study the difference in colloidal properties of various humic acids by measuring their viscosity (Vladychenskii, 1940). The humic acids separated from mountain peat soil showed strong hydrating properties and colloid structure formation, whereas those from black chernozem soils had little of these properties.

An investigation of particle size of humus colloids as related to viscosity (Beutelspacher, 1952) indicated that the humus particles are spherical. The particle weight is a function of the alkalinity of the solution, this weight, in solutions containing more than 1.25 equivalents of alkali, is about twice that in solutions containing less than 1.25 equivalents of alkali. The effect is believed to be reversible and is caused by hydrogen bonding of the elementary units. Coacervation, or coagulation to a more viscous phase, is believed to occur when a purified humus is placed in an acid medium. This coacervation results in a zeta potential (between the particles and the medium) of —23 mV, whereas in alkaline media, $\zeta = 0$. Alkali humates are, therefore, not stabilized by electric charge. The presence of nitrogenous humus in an acid medium produces a reducing agent. Such geological processes as the leaching of iron-coated sediments beneath coal beds and the transportation of elements of minerals as humates probably involve the phenomena described.

It has been stated that phosphate anions are strongly adsorbed by positively charged $Fe(OH)_3$ colloids, but far less strongly by negatively charged humus colloids (Aderikhin, 1947).

Properties of coagulation and peptization—Coagulation and peptization of ammoniacal humic acids from peat was studied by Apushkin (1935). These acids are reversibly coagulated by H_3PO_4, HCl, H_2SO_4, HNO_3, and reversibly peptized by alkalis but only very weakly by anions. The ability of the cations Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+} to coagulate depends on their position in the lyotropic series, i.e., their effect on the reactions in the colloidal solution. Sorption of NH_3 by humic acids in reactions involving NH_3 and H_3PO_4 was observed. Further study of the geological aspects of these reactions would be of interest.

Properties of adsorption in humus—When the adsorption on $Ba(OH)_2$ of humic acid and esterified humic acid were compared (Stadnikov, Syskov and Ushakova, 1935) similar limiting values were obtained owing to saponification of the ester by the adsorbed base. More complete esterification (methylation) of humic acid gives different limiting values of adsorption because it is believed that phenolic hydroxyls take part in salt formation.

The capillary conductivity of water in peat soils at relatively low capillary tension was measured (Richards and Wilson, 1936) and found to be greater than that reported for mineral soil. Furthermore, in peat soils conductivity of water is possible at lower tensions than in mineral soils.

Acid peats, such as *Sphagnum* peat, will adsorb as much as 20% of their dry weight of ammonia. The ions of other elements including P, K, Mg, Ca, and Fe, are also adsorbed by humus in varying amounts. Humus that is unsaturated with bases has been found capable of adsorbing base and liberating phosphoric acid from insoluble phosphates. (See also section on effects on solubility of transported inorganic ions.)

The peptizing effects of humus on clays is important in sedimentary geology. The peptizing action is followed by the formation of adsorbed humus coatings around the clay particles, which in turn retard the flocculating effects of the electrolytes on the clays. Ferric hydroxides are similarly protected by humus coatings.

A study was made of the relationship between humus content and "sorption" of N_2, O_2, and air in numerous soils, synthetic limonite, bog iron ore, ochre, synthetic hydrargillite, $Al(OH)_3$, clay, $CaCO_3$, shell limestone, gypsum, and $SiO_2 . H_2O$ (Weissman and Neumann, 1935); no conclusive relationship was found.

Absorption spectra—The absorption spectra of humic substances have been investigated by Gex and Firton (1944); and Hadži (1951). The *ultraviolet* absorption spectra of extracts of peat with water, dilute sodium hydroxide, dilute hydrochloric acid, and in part subsequent treatment with acid or methyl alcohol, showed several absorption bands (Gex and Firton, 1944). Aqueous extracts showed absorption at 275 mμ at pH 9.24; at 305 and 325 mμ at pH 10.37. Hydrochloric acid extracts had absorption bands at 275 and 325 mμ at pH 6.78; and at 275, 286 and 325 mμ at pH 7.00 and higher. The absorption of hydrochloric acid precipitates of sodium hydroxide extracts was strongest at 305 mμ with lesser absorption at 355 mμ. Methanol precipitates of the sodium hydroxide extracts showed absorption mainly at 286 mμ and lesser absorption at 305 and 355 mμ.

Ultraviolet absorption spectra of sugar solutions after heating, of hydroxymethylfurfural, and of humus substances prepared from sugars were obtained by Evstigneev and Nikiforova in 1950 (Fig. 2). Medicinal grade glucose shows only little absorption in the 300–400 mμ range, gradually increasing into the far ultraviolet but with no well-defined maxima. Hydroxymethylfurfural, a decomposition product of glucose, shows a characteristic absorption at 282.5 mμ and 228–230 mμ. (See also under "Humic materials in rocks".) Humic acid from sugars has initial absorption in the visible part of the spectrum, increasing abruptly in the ultraviolet without development of a maximum. When a 10% glucose solution is brought to a rapid boil, an increase in the ultraviolet absorption spectrum is observed. After boiling a few minutes, maxima appear at 280 and 230 mμ; on further boiling under reflux the maximum shifts from 280 to 280.5 mμ

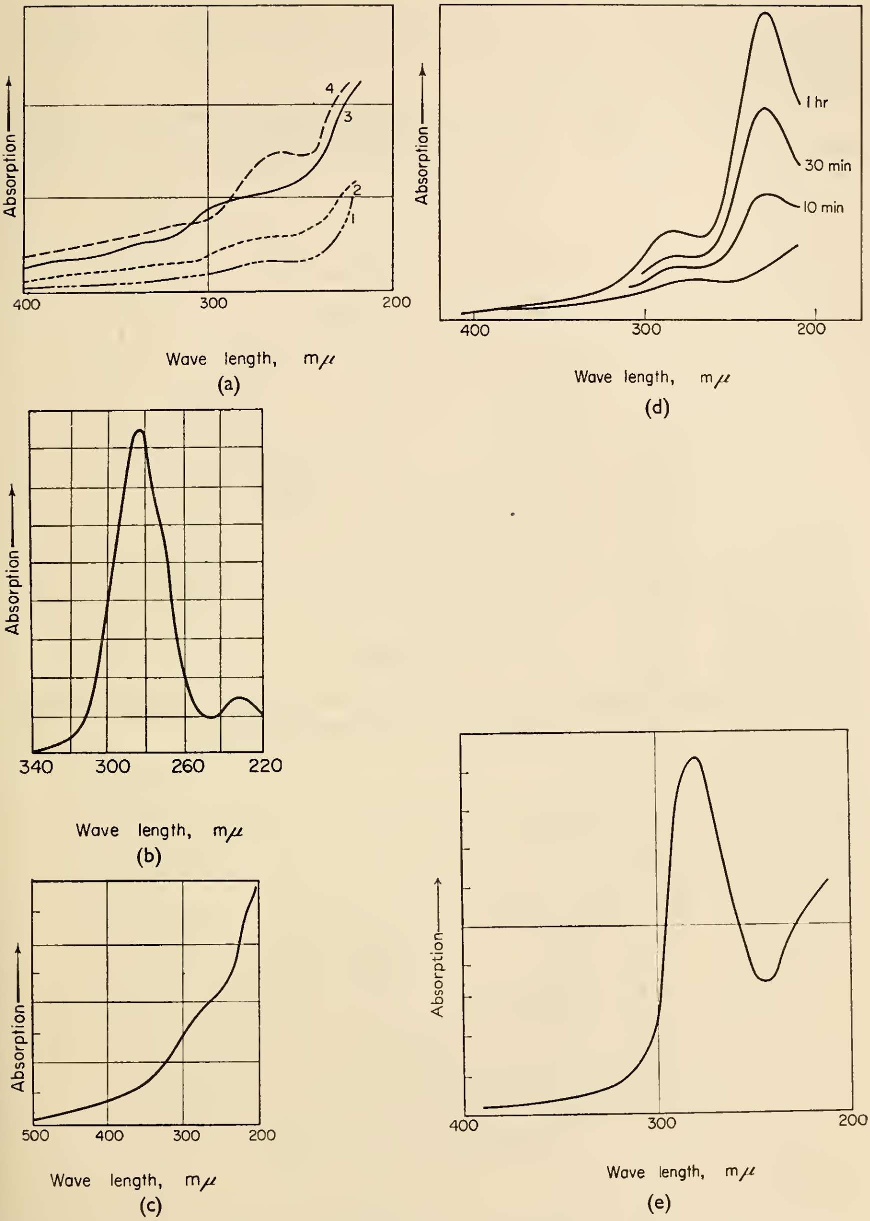


FIG. 2. a. Ultraviolet absorption spectra of solutions of sucrose and glucose (after Evstigneev and Nikiforova, 1950). 1, sucrose; 2, chemically pure sugar; 3, granulated sugar; 4, medicinal sugar.

b. Ultraviolet absorption spectrum of hydroxymethylfurfural (ibid.)

c. Ultraviolet absorption spectrum of humic acid (ibid.)

d. Ultraviolet absorption spectra of glucose solutions after boiling under reflux for different intervals of time.

e. Ultraviolet absorption spectrum of glucose solution after adding acid and further boiling.

and from then on does not change. Addition of acid does not affect the solution on further boiling under reflux until after 250 hours when the 230 mμ maximum disappears.

Ultraviolet absorption spectra of sulfuric acid hydrolyzates of humic acid, peat, lake copropel and bituminous Devonian and Precambrian

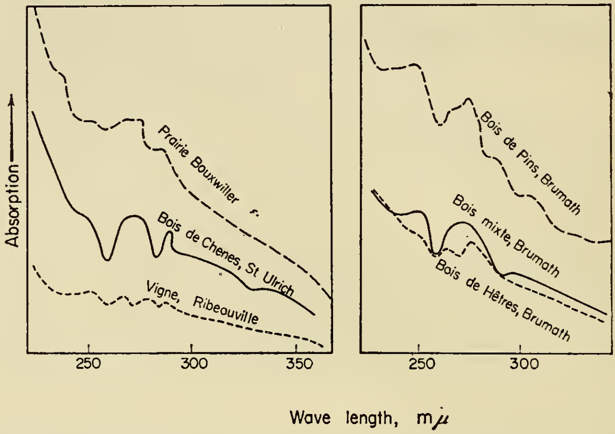


FIG. 3. Ultraviolet absorption spectra of aqueous extracts of soils from various terrains (after Vlès and Gex, 1943).

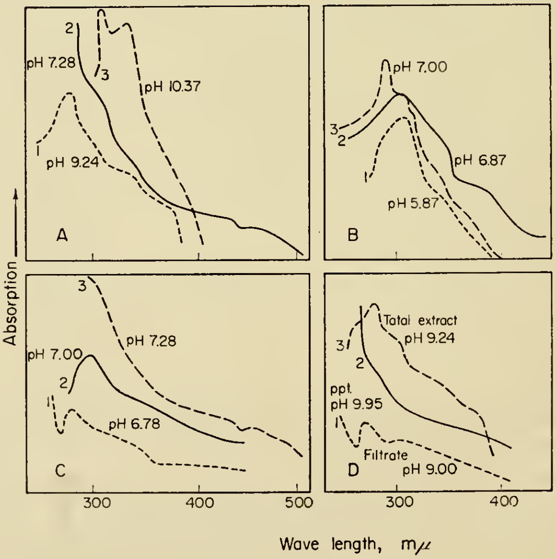


FIG. 4. Ultraviolet absorption spectra of peat extracts, adjusted to various pH values, as indicated (after Gex and Firton, 1943) A, sodium hydroxide extract; B, water extract; C. D, hydrochloric acid extracts.

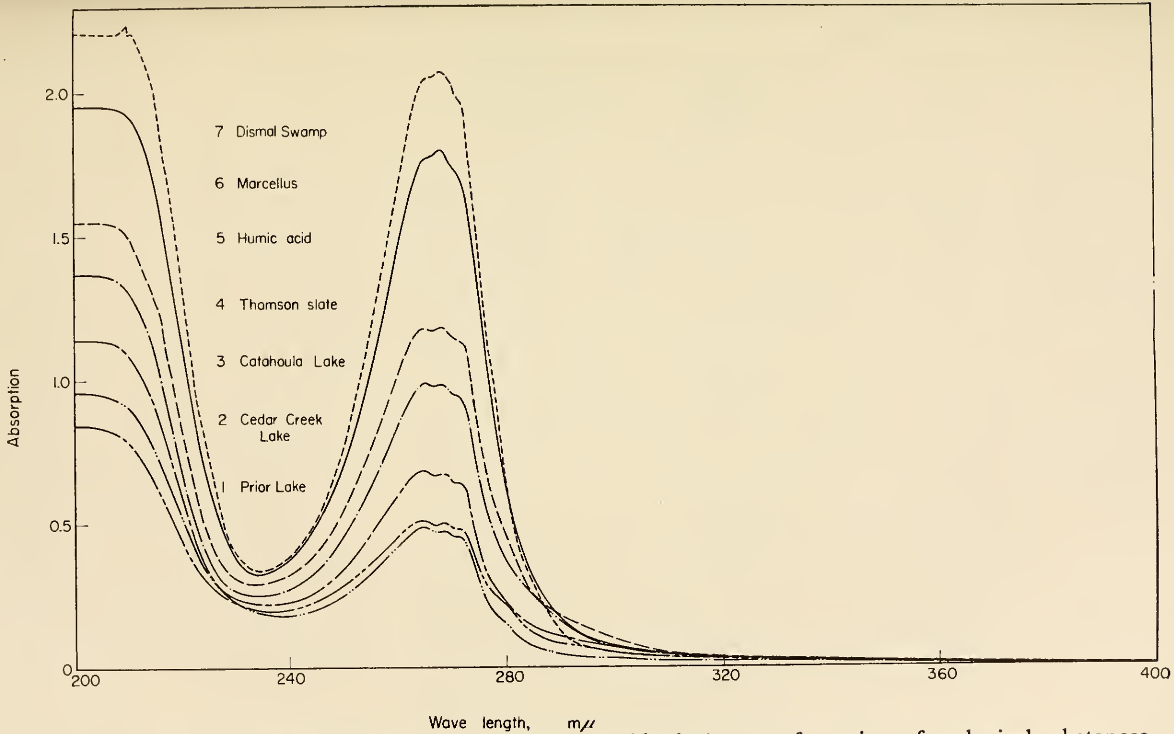


Fig. 5. Ultraviolet absorption spectra of sulfuric acid hydrolyzates of a variety of geological substances. 1, copropel from Prior Lake, Minnesota; 2, marly copropel from Cedar Creek Bog Lake, Minnesota; 3, copropelic silt from Catahoula Lake, Louisiana; 4, Thomson slate, early Precambrian, Minnesota; 5, humic acid prepared from Minnesota peat; 6, Marcellus black shale, Devonian, Pensylvania; 7, peat from Dismal Swamp, Virginia.

slate all have maxima at 268 mμ (Fig. 6). The identity of this material is as yet unknown.

The *infrared* absorption spectra of fractions of a benzene extract of coal and of tar pitch have also been obtained (Hadži, 1951). The extract soluble

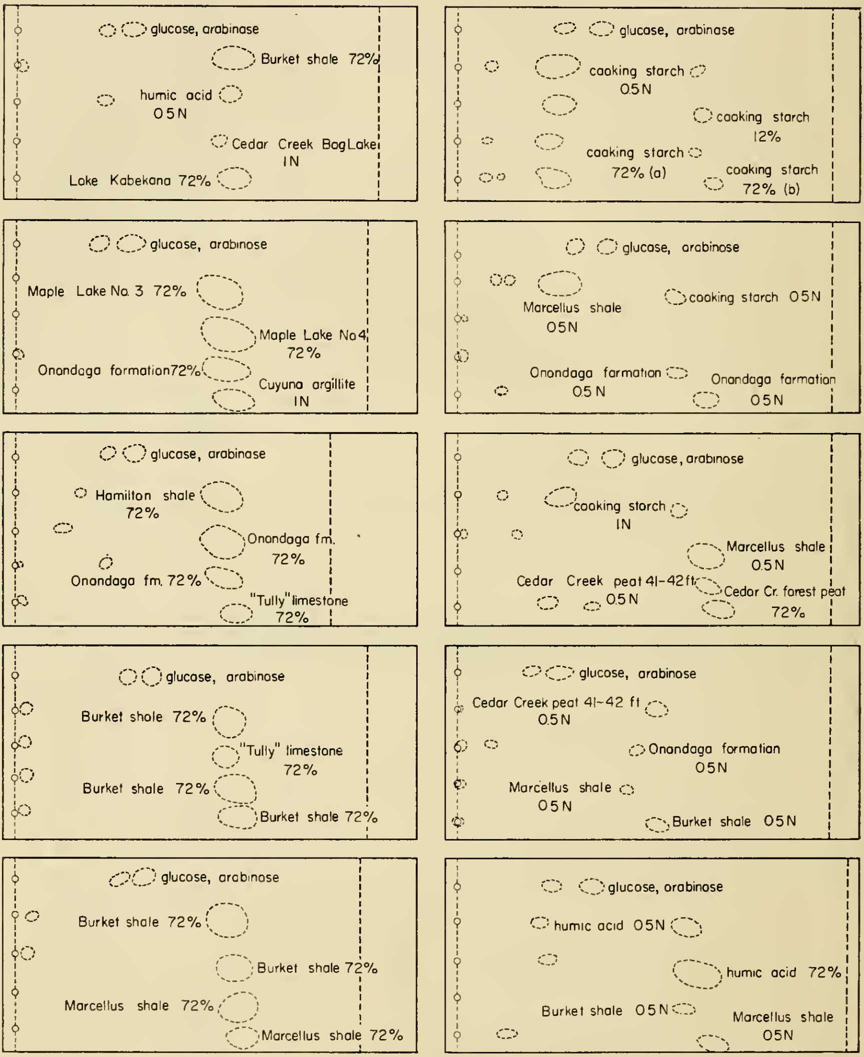


FIG. 6. Paper chromatograms of sulfuric acid hydrolyzates and extracts of cooking starch; modern lake sediments and peat from Minnesota; Devonian Onondaga limestone, Marcellus shale, Hamilton shale, "Tully" limestone and Burket shale from Pennsylvania; and later Precambrian Cuyuna argillite from Minnesota. Glucose and arabinose are spotted for reference on left-hand side of each chromatogram. Solvent, butanol: acetic acid: water (40 : 10 : 50). The substance having the high R_f value was eluted and, in ultraviolet absorption spectrum, showed prominent absorption in the region 264–272 mμ. (Swain, 1958, p. 2887).

in carbon tetrachloride was characterized by low content of aromatics and by high phenol content.

The infrared absorption spectra of humic acid prepared from North Dakota lignite (Wood *et al*, 1961) show that alcohol-benzene fractions of the humic acid are similar in their spectra to the residue of the humic acid. The intensity of the carbonyl absorption at 1720 cm^{-1} was appreciably greater in the fractions than in the residue.

X-Ray Investigation of Humus

X-ray investigations of humic substances, humic acid, coal, peat, and soil have been carried out; the X-ray diffraction patterns of both natural and artificial humic substances have provided evidence that their basic crystal structure is aromatic, and based on the graphite lattice.

Jodl (1941) reported his X-ray studies to show phenol humic acids to be submicrocrystalline, whereas carbohydrate humic acids were entirely amorphous. Natural humic acids were thought by him to be crystalline, and the similarity of their Röntgen interferences to those of phenol humic acids suggested a structural similarity of the two, i.e. lamellar dispersed systems. Jung's (1946) X-ray studies of lignite, peat, and black earth humus, and of the humic acids from these materials, were interpreted to show crystalline carbon to occur in most of them. Highmoor peat yielded only amorphous carbon, but the others had small amounts of crystalline carbon in an amorphous matrix. Debye–Sherrer photographs and electrical conductivity measurements of coked samples of humic acid were also made and reported to show that humic acids are not crystalline but consist of crystallites of graphitic structure in an amorphous to mesomorphous groundmass. More or less similar results were obtained by Agde and Jodl (1942) who suggested that the humic materials of brown coal are decomposition products of lignin.

Gorhanov (1947) disagreed with these interpretations, stating that mineral matter and salts obtained during extraction procedures are responsible for the Debye rings reported by others. Freshly prepared sodium and calcium humates did not show crystalline structure. The diffuse rings occurring in X-ray diffraction photographs of some humic acids, Gorhanov believed, result from intramolecular diffraction.

Available data suggest that the graphitic structure may appear in more or less aged humus as a result of condensation reactions of humus to humin and finally to graphite (see discussion of structure of humic acids). The degree to which graphitization may have occurred in individual samples is a function of source material, biochemical activity, temperature, and other factors (see Metamorphic Processes, Chapter 3).

Distribution and Types of Humus

The distribution of humus in nature was summarized by Waksman (1938) more or less under the following headings: (1) in composts of terrestial manures and plant residues; (2) in heath and forest soils; (3) in mineral soils; (4) in peat and coal; and (5) in water systems.

The *terrestrial manures* and *plant residues* are of less importance to the geologist than to the soil scientist, although water drainage from such accumulations may have geological significance. Because the carbohydrates, fats, and proteins are extensively utilized, animal excreta are enriched in lignin relative to the original plant substances. The manure of common livestock contains on the average (Waksman, 1938):

Ether soluble (fats, etc.)	2.49%
Cold water soluble (simple sugars)	9.13%
Hot water soluble (polysaccharides)	4.48%
Hemicellulose	20.18%
Cellulose	23.80%
Lignin	18.37%
Total nitrogen	2.51%
Ash	13.09%

The content of nitrogen, phosphorus, and potassium in manure of common livestock and barn fowl reflects the difference in food (Waksman, 1938):

	N	P_2O_5	K_2O
Livestock	2.86	1.84	1.42
Barnfowl	5.97	5.83	3.25

In compost the manure gains in lignin, protein, and mineral substance, and shows a decrease in fats, cellulose, xylan, and organic acids. The micro-organisms taking part in the decomposition include a host of fungi and bacteria, both aerobic and anaerobic (Waksman, 1938, p. 193). In straw-bearing manure, thermophilic bacteria bring about decomposition of cellulose and pentosan but not of lignin. The latter gives rise to dark brown humus substances that are slowly attacked by basidiomycetous fungi. The nitrogen liberated in decomposition of urea and other nitrogenous materials is in part synthesized and stored as proteins by micro-organisms. In part it may also be incorporated in the humic acid complex (Swain, Blumentals, and Millers, 1959).

Forest soils have been subdivided into distinct layers:

1. Litter, surface layer.
2. Duff, F, or intermediate layer, beneath the litter, in which the organic matter is undergoing active decomposition.
3. Humus, or H layer, in which decomposition has proceeded so far that original structure of the plant residues is unrecognizable.

In the process of decomposition the same relative changes in fats, carbohydrates, and proteins occur as in composts. Resins, and some other benzene–alcohol-soluble materials, proteins, and mineral matter are enriched. If *corrosion* (Waksman, 1938, p. 235) occurs, both cellulose and lignin are equally decomposed as in mull soils; the fungus *Agraricus nebularis* is effective in attacking pentosans as well as lignins. If *destruction* takes place, only the cellulose and hemicellulose are attacked while the lignin is preserved; the fungus *Coniophoria arebella* accomplishes this type of decomposition. Bacterial decomposition of partly decomposed cellulose leads to the formation of methane through the activity of *Methanosarcina* and other bacteria (Liebmann, 1950).

The chemical variations in one example of a forest soil profile, that at Keene, New Hampshire, are given in Table 1 (Waksman, 1935a).

TABLE 1.

Composition of a Forest Soil Profile from Keene, New Hampshire

Horizon	pH	Ign. loss %	Tot. Carbon %	Tot. Nitrogen %	C/N	Ether sol. %	Hot-water sol. %	Methanol sol. %
Litter	4.49	96.00	50.99	1.01	50.5	6.38	4.06	2.57
F-layer	4.23	83.04	43.63	1.60	27.0	4.86	6.73	4.16
H-layer	3.79	75.20	41.45	1.56	26.6	4.25	3.21	3.54
A_1	3.96	18.95	10.36	0.42	24.6	3.21	1.88	2.25
A_2 (bleached)	4.00	5.80	2.45	0.12	20.4	3.12	4.18	2.42
B_1	4.24	11.75	4.74	0.24	19.8	1.54	2.38	1.08
B_2 (passing into C)	4.26	9.90	3.27	4.10	32.7	1.00	1.03	0.98

The humus in a heath podsol profile is summarized in Table 2 (Weis, 1932).

TABLE 2.

Composition of Heath Podsol Profile

Horizon	Description	Depth cm	pH	Humus %	Nitrogen in humus %
A_1	Raw humus	8.9	3.6	27.03	1.81
A_1–A_2	Trans. to bleached sol.	12.7	—	—	—
A_2	Pure bleached sand	19.7	3.9	1.78	1.68
A_3	Humus hardpan	27.1	4.1	12.65	2.29
B_1	Iron hardpan	33.3	4.5	2.65	2.30
B_2	Trans. to parent material	67.7	—	—	—
C	Parent material	135.5	4.8	0.24	2.08

The variable factors in development of forest humus, i.e. variation in climate, soil structure, microbial population, etc., have been exhaustively discussed by Waksman (1938). Emphasis is laid on the differences in the humus from coniferous and deciduous litter. The needles and other products of coniferous origin are decomposed mainly by fungi that reduce the celluloses and hemicelluloses but not the lignin; the resultant mat is low in bases and in nitrogen of acidic nature, decomposes slowly, and is easily leached. The deciduous litter, on the other hand, is decomposed by a great variety of fungi, bacteria, and invertebrates; this type of humus is high in bases and in protein bound together in stable lignoprotein complexes, and is less acid than the coniferous type. The geologic products resulting from the drainage through these different types of humus would obviously be different. The pre-Cretaceous humic run-off fractions would be of different composition than those of the Cretaceous and younger deposits in which deciduous plants play a part.

Determination of the humus content in mineral soils, i.e. those containing silicate and carbonate minerals in considerable abundance, is subject to several errors. After correction for the amount of carbon dioxide evolved from the carbonate minerals and for the combined water from the silicates, sulfur, and other volatiles, the loss on ignition above 1000°C is taken as the total organic carbon. This figure multiplied by 1.724 (Waksman, 1938) gives the humus content. Various attempts to improve this figure by modified procedures, use of total nitrogen multiplied by the factor 16, and other methods have not improved the combustion-carbon procedure. The humus value is at best an approximation.

The amount of humus in soils varies from 0.5 to 10%, that of black soils or chernozems is considerably higher than gray serozems, brown chestnuts, or red kraznozems. The humus : nitrogen ratio is 16.9 : 1 to 21.2 : 1 in surface soils and 15.6 : 1 to 21.4 : 1 in subsoil. In humid regions the humus is more or less concentrated in a thin surface layer; in arid regions it is more or less uniformly distributed to considerable depths. Soil humus is for the most part more highly altered from the original plant materials than other types of humus. Lignins and their derivatives and proteins form the predominant substances, together with hemicelluloses, lipoids, and small quantities of other constituents. Waksman (1938) has described in detail the features of soil humus.

Humus in *peat* has received more attention than the other types. Peat is a layer of largely organic matter formed of plant and animal residues and other products partly or entirely submerged in water (Waksman, 1938, p. 262).

Several varieties of peat have been recognized based on geologic and limnologic setting and flora. *Lowmoor* peats are composed mainly of sedges and reeds, together with certain trees and shrubs; are characterized by low cellulose content, low acidity, high ash and nitrogen; and are formed when drainage from calcareous rocks or soil flows into shallow undrained depressions. *Highmoor* peats consist of *Sphagnum* and other mosses formed on crystalline rocks, mineral-poor soils, or on other types of peat in upland seasonally drained terranes in cool wet climates. They possess high acidity, cellulose, and hemicellulose, and low ash and nitrogen content.

Forest peat is made up of trees and certain lower plants, frequently with a carpet of *Sphagnum* mosses. In Cedar Creek Bog, Minnesota, the lowmoor peat is developed about a late eutrophic or dystrophic bog, and forest peat of white cedar and other trees surround the lowmoor zone (Lindeman, 1941b).

Sedimentary or *lake peat* consists primarily of settled plankton, together with aquatic plant debris, aquatic arthropods and other finely divided material. *Copropel* or *gyttja* is gray or brown, liver-textured, and forms in the epilimnion and thermocline, and in the hypolimnion zones of oxygenated lake basins. *Ävja* is a term applied to accumulations primarily of settled plankton. *Sapropel* is black and forms in prolonged de-oxygenated hypolimnotic zones. *Dy* is precipitated colloidal humus, generally mixed with other types, but occurring abundantly in muskeg lakes of the higher latitudes.

A dark brown to black gelatinous substance, *dopplerite*, occurs at depth in some bog and marsh deposits. It is of the same nature as humic acids, being soluble in dilute alkali, and is precipitated by acid. It contains up to 58% carbon, up to 5% hydrogen, 40% oxygen, 1–2% nitrogen and 3.5–5% ash. It is believed to represent the result of ground water concentration of the black jellylike substance (phytocollite) formed in decomposing plant materials. The colloidal "*dy*" and "*humolimnic acids*" (Shapiro, 1957) of northern lake and river waters may be of this nature.

Humic substances can be extracted from lower ranks of coal by alkalis and this has been variously called humic acid, ulmic acid, humin, and ulmin. Humus of peaty nature doubtless has been the parent material for most beds of coal.

The humus of *rivers*, *lakes*, and *seas* is partly of allochthonous and partly of autochthonous nature. Whereas the major contributors to terrestrial humus are higher plants consisting principally of cellulose and lignin, humus in lakes and the ocean originates from diatoms and algae composed mainly of proteins and hemicellulose. The amount of humus that will accumulate on the floor of a lake or ocean is mainly governed by the ratio of producers to consumers in the body of water and in the accumulating sediments. Limnologists (Birge and Juday, 1922; Lindeman, 1941a; Roelefs, 1944) have assembled information on the net amount of organic accumulation in a variety of lakes. Lindeman (1941a) found, for example, a ratio of producers to consumers of 70.3 to 8.3 calories per cm^2 in a highly productive pond. In Lake Mendota, Wisconsin, the plankton (actually seston) comprised 8.37% N or 52.31% protein, 11.78% lipoids, 2.77% pentosans, 6.54% crude fiber (cellulose) and the balance mainly other carbohydrates. Roelefs (1944) used as an index of productivity a comparison between plant yield in pounds per acre and nutrient content (phosphorus, potassium, iron, calcium) of the water. He found that a lake bottom consisting of a mixture of organic matter and marl was the most highly productive of benthonic plants.

The importance of the stage of nutrient development of the lake waters to the total organic productivity has been emphasized by several writers (Lindeman, 1941a; Swain, 1956).

Marine humus is probably more nearly comparable to that of oligotrophic than to eutrophic lakes in composition. Marine plankton samples have been reported to contain 14–48% carbon, 1.5–10.6% nitrogen, and 13–65% ash (Brandt, 1919).

Processes of Humus Formation

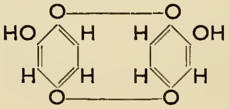
Humus formation mainly by nonbiological processes—The concepts of the origin of humus can be roughly divided into the purely chemical and the purely biochemical theories, although in several instances separation of the two is difficult.

A progressive early chemical theory was that of Beckley (1921), who proposed that the action of mineral acids on carbohydrates forms hydroxymethylfurfural which, on condensation, may produce humus. Although this theory has been discarded on the grounds that concentrated mineral acids do not occur under natural conditions (Waksman, 1938, p. 105), it is now known that sulfuric acid may be present in lake bottoms (Frey, 1949, p. 22) and, given the geologic time factor, could conceivably produce small amounts of furfurals.

Another chemical theory is that of condensation of carbohydrates with amino acids or polypeptides (Waksman, 1938, p. 105). This stems from the recognition by Eggertz (1888) and Andre (1898–99) of the essential role that nitrogen plays in humus. In stable manures ammonia was believed to act upon lignin-like materials to produce humus; the associated micro-organisms aided in the hydrolysis of proteins to polypeptides and of amino acids and complex carbohydrates to sugars, but otherwise played only a minor part in humus formation.

The oxidation of aromatic compounds was offered as another explanation for the formation of humus. Eller (1922) found that when phenol, quinone, and hydroquinone were oxidized in alkaline solutions dark colored products were formed which resemble natural humus.

Eller (1922) and Leopold (1928) pointed out that the "humic acids" obtained from carbohydrates are different from natural products in chemical (carbonyl member, etc.) and physical properties. On the other hand, oxidation of phenols and their derivatives are closely similar in their properties to natural humic acids. The chlorine derivatives of phenol humic acids and natural humic acids contained 42–44% chlorine, were easily soluble in alcohol, ether, phenol, and acetic acid, were destroyed on boiling with water and on treatment with cold potassium hydroxide solution. The chlorine derivatives of carbohydrate "humic acid" contain only 23% chlorine, were incompletely soluble in alcohol, were mostly insoluble in the other solvents, and were resistant to hot water and to cold alkaline solution. Eller considered the artificial phenol humic acids to have the formula $x(C_6H_4O_3)_2$ with a micelle structure as follows:



He thought that natural humic acids, however, originated by the oxidation of hexose.

$$C_6H_{12}O_6 + O \rightarrow C_6H_4O_3 + 4H_2O$$

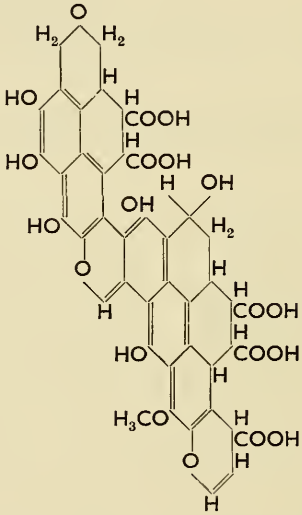
According to Kashirskikh (1940), humic substances are formed by the condensation of decomposition products of carbohydrates (which apparentlv belong to furan derivatives) with themselves or with hydrolysis products of albumin.

A scheme for the formation of humic acids was outlined by Enders and Sigurdsson (1943) in which an early step was postulated as an aldol condensation of methylglyoxal under the influence of amino compounds in the soil. Mixtures of methylglyoxal (CH_3COCHO) and glycocoll (glycine, NH_2CH_2COOH) in water formed "melanoidin" with accompanying decrease in carbonyl-group content. Methylglyoxal alone underwent no reduction of carbonyl nor formed melanoidin. No carbon dioxide is evolved in the melanoidin reaction with glycocoll, and no Schiff-base type of compound or pyrrole ring is produced. Mechanism of the process is uncertain, particularly as to how the nitrogen enters the humic acid micelle.

Aleksandrova (1951) pointed out that humus formation need not be from lignin because algae, lichens, and mosses in which lignin is absent also give rise to humus.

Breger and Whitehead (1951), by means of differential thermal analysis, furnished evidence that lignin may be traced through peat into lignite, although the low temperature characteristics of lignin disappear or are suppressed in peat and reappear in lignite. There is a sharp exothermic peak for lignin at 425°C; a humic acid component of peat has an exothermic peak at 435°C, and bituminous coal also has exothermic peaks somewhat above 425°C. Whitehead and Breger believe that this upward shifting of the peak is the result of devolatization of the humic materials and from their polymerization or condensation into a more stable structure which decomposes at a higher temperature. Varossieau and Breger (1951) believe that lignin is the parent material of much of humic acid. In their study of wood degradation in piling exposed when Rotterdam was bombed in 1940, Varossieau and Breger found an increase in lignin and loss of cellulose in outer layers of the piling. The methoxyl contents of the exposed lignin are subnormal compared to those deeper in the piling. Demethylation is known to take place during the decomposition of plants, and peat is known to have a methoxyl content of only about 1%. This process may involve a biochemical removal of methyl groups from lignin, leading to formation of methane and phenolic hydroxyl groups. Breger (1951, p. 206) postulates that only one transformation in a structural unit of lignin need occur to produce acidic properties. If multiple conversions were to take place along the lignin molecules in the chain, together with cleavage of the chain through formation of carboxyl groups, the various humic substances might well be formed (see Chapter 3).

Lange (1890), Hoffmeister (1896), Fischer (1921) and others stressed the role of lignin in the formation of humus. The phenyl ring of lignin, containing acetyl and methoxyl groups, was believed to lose the acetyl groups during humification; an increase in the size of the molecule by oxidation or by dehydration would result in the formation of alkali-insoluble humin and then coal (Jonas, 1921; Simek, 1928). It is a tribute to these workers that their ideas are closely similar to present concepts of the origin of humic acid. It was concluded by Fuchs (1931) that the humic acid molecule contains 3 to 4 carboxyl groups, 3 to 4 hydroxyl groups subject to methylation, one methoxyl group, and one carbonyl group. The decomposition of dead organic material formed a group of natural oxy-carbonic humic acids, dark amorphous substances capable of yielding hydrogen ions, of forming salts, and of having base exchange capacity. The nitrogen, which can be cyclically bound up in humic acid on treatment with ammonia, was thought by Fuchs to be polypeptide in nature. He suggested the following formula:

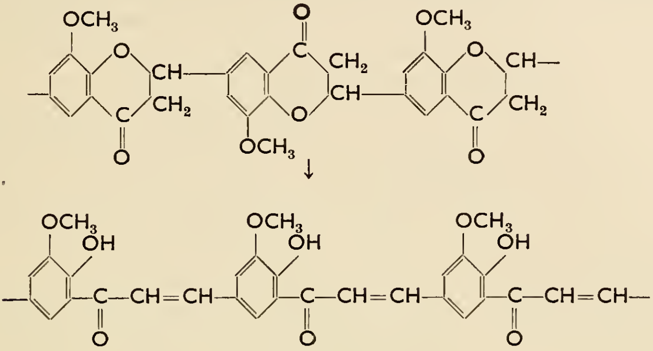


The fact that peat humic acids are more acid and give lower equivalent weights than those calculated on the basis of the carboxyl content (Stadnikov and Korschew, 1929) led to the suggestion that phenolic groups provide these effects. The acidity of "humic acid" was, therefore, thought to result from the content of carboxyl and phenolic hydroxyl groups; the latter are partly transformed to ether groups.

The molecular weights of alcohol soluble (hymatomelanic) acid and alcohol-insoluble (humic) acid preparations were determined by Samec and Pirkmaier (1930) as follows: humic acid from lignite 1445, from peat 1235, from "brown coal" 1345; hymatomelanic acid from lignite 855, from peat 761, and from brown coal 739. These figures have no real value except to indicate roughly the degree of polymerization or condensation of the humic substances.

Naturally occurring Cassel brown coal and dopplerite have been thought of as nearly pure humus because of their insolubility in acetyl bromide and solubility in sodium hydroxide solutions. Dopplerite is believed to form when humic acid solutions come in contact with calcium carbonate.

Breger (1951) suggested that humic acid can develop from lignin (Russell lignin was used as a model substance) by opening of the heterocyclic ring:

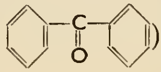


The "humic acid" structure contains phenyl rings, acidic phenolic hydroxyl groups, double bonds, and a structure based on phenylpropane, all of which are believed to occur in lignin structures. Comparisons of infrared absorption spectra of spruce wood lignin and of humic acid from peat gave results shown in Table 3.

TABLE 3.

Correlation of Infrared Absorption Peaks for Humic Acid and Braun's Native Spruce Lignin (*after Breger*, 1951)

Substance	Position of absorption peaks, microns
Humic acid, low concentration	4.3, 4.6, 4.9, 5.3, 5.9, 6.2, 8.8, 9.1, 9.7, 10.3
Humic acid, high concentration	3.0, 3.8, 4.3, 5.9, 6.2, 8.1, 9.7
Braun's native spruce lignin	3.0, 4.3, 5.8, 6.1, 6.25, 6.6, 7.9, 8.2, 8.8, 9.2, 9.7, 10.8, 11.7

Breger suggests that the absorption maxima at 3.0, 7.9 and 8.1 μ result at least in part from the presence of phenolic hydroxyl groups (attached directly to an unsaturated carbon atom, i.e. C=C(OH)—). The 5.9 μ peak suggests a carbonyl stretching structure. The peaks at 8.1 or 8.2 μ imply aromatic ketone groups (i.e. *benzophenone* ); and those at 8.8 μ suggest aliphatic ketone groups. The peak at 9.7 μ may indicate multiple substitution on benzene rings. From a comparison of the lignin and humic acid units, Breger suggests that the structures are related or perhaps identical.

By means of absorption spectra, Kumoda and Miyazato (1955) studied the effect of addition of various compounds on the formation of artificial humus from glucose. The yield of humus from glucose was found to increase after addition of hydrochloric acid and to decrease when hydroxylamine and amino acids containing benzene rings were added. Ammonium salts produced little or no effect on the artificial humus. Humus from glucose to which urea ($CO(HN_2)_2$) had been added was found to contain nitrogen. The absorption spectra of artificial humic acid, of extractions of it, and of soil humic acid are stated to be similar. The artificial humic acids heated with either hydrochloric acid or sodium hydroxide had similar absorption curves, but those treated with sulfuric acid were different, particularly in the ultraviolet region. Hydroquinone humic acids differ in their absorption spectra from glucose humic acids after each was treated with sodium hydroxide. When "alkali lignin" was treated with boiling hydrochloric acid (1 : 1), its light absorption increased in intensity, especially in the visible region. The presence of nitrogen apparently produces no effect in the absorption spectra of artificial humic acids.

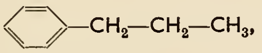
Biochemical aspects of humus formation—It was not until the last decades of the 19th century that meaningful data on the role of microorganisms in the formation of humus began to accumulate. The literature on the early work in this field was thoroughly reviewed by Waksman (1938, p. 102ff). Fungi were realized to be important in the production of humus from roots and leaves. Differences in the products resulting from aerobic versus anaerobic decomposition of organic matter were recognized. Proteinaceous material was shown to give rise to nitrogen-bearing humus; carbohydrates and organic acids produced nitrogen-free humus. It was observed that humic materials could be obtained by decomposition from almost all types of organic matter, although cellulose mainly was transformed into carbon dioxide and methane and yielded little, if any, humus.

Phenolic substances formed by decomposition of proteins were shown to be responsible for many of the dark colored materials in humus, and a similar process of oxidation of plant lignin, which contains a quinone or polyphenol structures to humus-like oxyquinones was suggested.

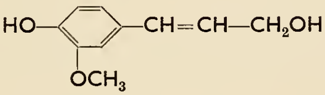
Certain microorganisms are capable of producing dark colored "humic" substances. *Actinomyces chromogenus* is able to produce quinone (Beijerinck, 1900). *Bacterium mesentericus* forms a black coloration due to benzenoid ring compounds, perhaps o- and p-dihydroxybenzene, which appear to give condensation products with amino acids (Muschel, 1922); dark colored substances also form when salts of benzoic and salicylic acids and phenol are decomposed aerobically by fungi and bacteria (*Bacterium pyocyaneum*).

Waksman advanced a formal microbiological theory for the formation of humus in 1927. The carbohydrate serves as the source of energy for the micro-organisms, the protein and hemicellulose cell substance is synthesized, and these products together with modified lignin form the bulk of humus. Further comprehensive discussion of the humic materials originating from various sources materials is given by Waksman (1938, p. 107–129).

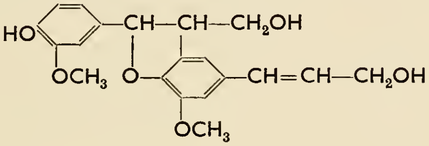
The understanding of the chemical nature of lignin stems from the work of Klason (1931). The basic unit of lignin is believed to be phenylpropane (Fraser, 1955, p. 55).



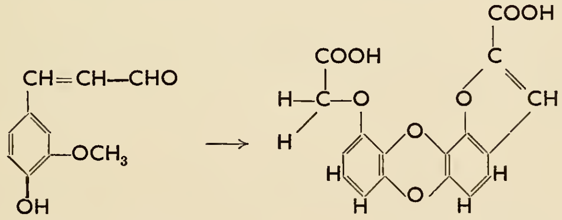
which is related to coniferyl alcohol



A dimer, dihydroconiferyl alcohol is found in old spruce wood:



A suggestion as to the origin of "lignohumic acid" from coniferyl-*p*-aldehyde was made by Oden and Lindberg (1926):



Coniferyl-*p*-aldehyde "Lignohumic acid"

The biological aspect of humus formation has also been studied in detail in recent years.

Formation of humus by micro-organisms is believed to involve mainly micro-organisms that have undergone autolysis (Enders, 1943), i.e., solution in their own fluids. Conditions under which autolysis is promoted were studied and it was found that daily and annual climatic variations provide the required factors for autolysis of micro-organisms in soil. Thus the objections that humifying processes require some unnatural physical conditions can be overcome.

The part played by cellulosolytic myxobacteria in humus formation was investigated by Konsnova (1949) and Küster (1953). Lignin-derived polyphenols are believed to undergo oxidation with the aid of peroxidase or polyphenoloxidase originating from cellulosolytic actinomycetes, myxobacteria, or fungi. These oxidation products are then thought to condense with bacterial proteins or their degradation products to form humic acids and humus. The degradation products of cellulose are functional in the process after they have been assimilated by bacterial cell plasma.

An investigation of the humus-forming properties of flavobacteria was made by Benetti and Schiesser (1950). Five species of *Flavobacterium* were isolated, some of which utilized phenol and phenolic compounds, such as resorcinol, pyrocatechol, phloroglucinol and sodium salicylate, as their only sources of carbon. When sodium acetate or some derivative of the fatty series was added to the culture, a brownish-black material similar to soil humus was formed.

Autolysis was believed to have occurred when various strains of *Actinomyces* isolated from calcareous soil (pH 7.2) formed dark brown substances (Scheffer *et al.*, 1950). The process was viewed as one of autoxidation followed by condensation or polymerization. Glutamic acid and glycine produced the highest yields of humic substance. Ultraviolet absorption spectra of these materials were stated to be like those of humic acids, showing a quinone structure like gray humic acid. The quinonoid substances probably originated as metabolic products of the microorganisms.

Another study involving *Streptomyces* was made (Küster, 1953) in which cultures were grown in many different media including 32 different amino acids. Of these, humin substances were found with glycine, serine, theonine, valine, leucine, isoleucine, arginine, lysine, glutamic acid, methionine, phenylalanine, tyrosine, tryptophan and hydroxyproline.

Benzoic acid, (C_6H_5COOH), when metabolized by *Azotobacter*, formed a black humus-like substance through the action of a benzoctase (Pochon and Tsu Long Wong, 1950). When several species of fungi, actinomycetes, and bacteria were cultured in various nutrient solutions, all produced dark brown humic substances that were precipitated in acid solution (Plotho, 1950). Humus was not formed when the final pH of the solution was below 7.5. Preference as to nitrogen source was exhibited: *Aspergillus* preferred sodium nitrate, *Actinomyces*, glutamic acid, and the bacteria, glutamic acid.

Pigments were isolated from *Aspergillus* and from *Actinomyces* (actinorhodin) and on exposure to atmospheric oxygen humic acid formed from the pigment (Plotho, 1951) which contained 9% nitrogen and 2% sulfur, and was similar to pigment isolated from forest soil but different from that from tilled soil. Uronic acids were produced from cellulose by *Stachybotrys lobatula*, *Aspergillus fumigatus*, and *Alternaria tenuis*. Humic substances appeared only in alkaline media with *Stachybotrys*; *Alternaria* formed no humus. Furfural was reported to be produced intermediate between cellulose and humus. Glucuronic acid ($C_5H_6(OH)_5COOH$)

was converted to humic acid by several species of aspergilli, actinomycetes, penicillia, and fusaria; no humic acids were formed, however, from sorbitol, glucose, gluconic and saccharic acids. These humic acids contained 5.6–9.4% nitrogen and 1.2–2.3% sulfur.

A valuable systematic study of bacterial decomposition of plant residues in peat bogs was made by Isotulo (1951). The pH values of the *Sphagnum* and *Carex* peats studied were found to range from 3.3 to 4.3 and from 4.3 to 5.6, respectively, but with the progress of decomposition the pH in both types rose. Eh values in the surface layers were about 500 mV at pH 5; below 40 cm Eh values varied between +300 and −100 mV. After drainage and cultivation, Eh rose appreciably in the surface layers. Advance in humification of the *Sphagnum* and *Carex* peats increased the total nitrogen, ether-soluble material, lignin, and protein, whereas water-soluble organic material, water-soluble nitrogen, hemicellulose, and cellulose decreased; there was also a decrease in the ratio of available carbon and nitrogen. Burned-over moorland was characterized by a three-fold increase of ash at the surface, total nitrogen increased 1.5–2-fold at depths of 0–20 cm, and water-soluble nitrogen even more. As a result, microbial decomposition of hemicellulose and cellulose is favored at the surface. Bacilli are probably the most abundant micro-organisms in peat bogs. Two strains of anaerobic cellulose-decomposing bacteria from *Sphagnum* peat were isolated, one type had gram-positive, and the other type gram-negative, vegetative cells. At pH 7–7.5 the most rapid decomposition of cellulose occurred at 35–40°C, but continued as low as 5°C. Various sugars also were fermented. Yeast or asparagine favored the bacterial growth, but nitrates did not. The Eh of the gram-negative culture during decomposition of cellulose was −150 mV, and that of the gram-positive culture was −300 mV. Addition of reducing substances such as Fe^{++}, ascorbic acid, cysteine-HCl, etc., reduced the Eh of the culture sufficiently to support growth. The following fermentation products were obtained:

TABLE 4.
Decomposition of Cellulose by Bacteria from Sphagnum Peat

Medium	Gram-negative strain (%)	Gram-positive strain (%)
Acetic acid	44.1–68.91	47.6–49.5
Butyric and higher volatile acids	26.3–49.6	0
Lactic acid	0–2.19	4.7–8.4
Ethanol	2.1–6.3	37.2–39.8
Formic acid	0	6.0–7.4
Gaseous products		
CH_4	73.4	23.2
H_2	16.3	72.2
CO_2	10.3	4.6

In the formation of "sapropel" it has been suggested that the first stage in the degradation of the organic matter occurs at various depths in the sea water (Kuznetsov, 1951). Additional changes occur in the settled organic matter to depths of 60–100 cm. The decomposition products are fats, amino acids, humus, and gases: CO_2, H_2, CH_4, N_2, NH_3, and H_2S. The stable sapropel layer below the mud, Kuznetsov believes, is typified by slow change toward formation of bitumens.

Flask experiments were performed to follow the course of organic decomposition of various materials under both aerobic and anaerobic conditions for a four year period (Springer and Lehner, 1952). The rate of decomposition under aerobic conditions of various materials was as follows: green vegetation > straw > leaves > pine needles > peat > moss >highmoor peat. Disappearance of water-soluble carbohydrates and pectins was accompanied by an increase in lignins and humic acids. The authors state that intensive humus formation occurred during the first month and humus substances were highest after 1–2 years. The green vegetation and some of the other plants yielded a quantity of base-bound humus. Under anaerobic conditions decomposition was slower and more humus formed, also, there were increased numbers of micro-organisms.

An investigation of the incidence and role of micro-organisms in primitive soils was conducted by Aleksandrova (1953). Three soils were studied: melkozem (a primitive soil stage containing minerals) underlying mosses and developed on serpentines and diorites; a primitive rocky-meadow soil underlying grain-grass; and melkozem underlying lichens and developed on granite. The calcium content of the soil varied from 3.4 to 76.0 meq./100 g. of soil; magnesium, 3.4 to 31.2 meq./100 g.; pH from 5 to 6.5; organic matter, 10–42%; $N < 1\%$; and C : N ratios, 10–12. In progressing from lichen-covered to mossy to grass-covered soils there was a gradual increase in the number of putrefactive organisms (0.4 to 41.0×10^6/g of soil) and in *Actinomyces* (0.16 to 40.0×10^6/g); neither aerobic nor anaerobic nitrifying bacteria were more than weakly developed; fungi (*Dematium*, *Trichoderma*, etc.) were present but latent; lignin apparently was absent. Newly formed humic acids were found to show great stimulant effect on catalase and peroxidase activity in *Bacillus luteus* and *Bacterium mycoides* and in *Sorangium cellulosum.*

Barghoorn (1949) examined plant residues from several geological horizons and found a correlation between degradation of the plant tissues and fundamental structures of the plant cell wall; certain cell wall residues are persistent under anaerobic conditions and are found in petrifications. Non-cellulosic organic complexes, he found, are the principal contributors to fossil organic matter.

Breger (1949) examined evidence for the production and preservation of organic materials in terrestrial sediments. Deserts and arctic regions play no important part. In temperate and subtropical regions fungi and aerobic bacteria rapidly destroy cellulose. After burial the organic residues are attacked by anaerobic bacteria especially of the thermophilic type.

Lignin is an important contributor to humus; hydrolysis may lead to the opening of the heterocyclic lignin ring and lead to the formation of acid phenolic groups.

Specific Studies on the Components of Humus

General studies—Investigation of natural as compared to artificial humus showed humus from amino acids (glycine, tyrosine, cystine) and dextrose to contain more carbon and less nitrogen than natural humus (Liesche, 1928). The source materials of humus have been considered to be lignins, and humus was believed (Stoklass, 1929) to be a mixture of lignocellulose and decomposed and non-decomposed lignins with the cellular substance of bacteria. When certain humus is dried below 110°C it was found to agree in composition with that of galacturonic acid obtained by the hydrolysis of pectin (Aschan, 1932).

Study of the rate of formation of humic substance from sugars by acid extraction at 20°C (Smirnov, 1951) showed that the rate of humification is formally that of an equation of the first order. The yield increases in the order glucose, galactose, arabinose, and xylose; using 61.6%, 72%, and 78% sulfuric acid.

The origin of *humins* formed during the acid hydrolysis of protein was studied by Lillevik and Sandstrom (1941); thiazolidine-4-carboxylic acid is hydrolyzed to formaldehyde and cysteine on boiling for 24 hours with 20% hydrochloric acid.

Comparison was made between the combination of proteins with tanning agents and the formation of humic components of peat (Kurbatov, 1934). These components were visualized as a polymeric series comprising protein complexes and the products of their biochemical decomposition in combination with products of biochemical decomposition of lignin. The mixed-polymer nature of humic acid was advocated by Flaig (1955b) who believed lignin to be the source material. The chemistry postulated in the formation of humic acids from lignin (Flaig, 1955b) involves the demethylation of lignin to form certain polyhydric phenols; these phenols in alkaline solution may be oxidized to hydroxyquinones which then polymerize and are oxidized further undergoing ring fission to form dicarboxylic acids.

Kosaka and Honda (1955) showed upland soils of the A° horizon to be low and lowland soils to be high in humic acids.

Glycerol ($CH_2OHCHOHCH_2OH$), derived from vegetable and animal fats by decomposition, was visualized to be an important agglutinating agent of humic acids from various sources by Khrisanfova (1950).

Comparison of the constituents of alkali extracts of Ontario lignite and sugar humic acid prepared from sucrose with 72% sulphuric acid showed marked differences in the two acids (Souci and Quentin, 1954). The lignite extract had the empirical formula $(C_{82}H_{69}O_{28})_x$, while that of the sugar humic acid was $(C_{59}H_{49}O_{23})$ or $C_{55}H_{41}O_{11}(OH)_4(CO_2H)_2$. Methylation and acetylation of humic acids yield derivatives of different kinds and amounts. From this information it may be assumed that other materials than sugars were the major sources of the lignite.

Isolation of organic compounds from humus from sewage plants has resulted (Wedgwood, 1952) in the identification of polycyclic hydrocarbons, including pyrene, ($C_{16}H_{10}$), fluoranthene, ($C_{16}H_{10}$), 1,2-benzathracene, 3,4-benzopyrene, perylene, and ananthrene (a six ring compound), chlorophylls, and carotenoids.

The approximate percentages of certain groups in humic acid and coal were determined as follows (Chavalbury and Biswas, 1942): humic acid—total hydroxyl, 6.4%; phenolic hydroxyl, 6.2%; alcoholic hydroxyl, 0.2%; carboxyl, 23–25%; and carbonyl, 3.54%: coal—total hydroxyl, 2.1%; phenolic hydroxyl, 0.1%; alcoholic hydroxyl, 2%; carboxyl, 0.9–5%; and carbonyl, 0.12%. The humic acid contained oxygen unaccounted for, probably as ether or cyclic oxygen. Using a ratio of 2 : 6 : 9 :: carbonyl : hydroxyl : carboxyl groups in humic acid, the molecular weight was calculated to be 1600.

Armstrong and Piret (1947) determined that $KMnO_4$ oxidation of peat in an alkaline solution produced about 10% of aromatic acids, which were mainly polycarboxylic.

Carbohydrates and related substances—Methylated sugars were isolated from hydrolyzates of a soluble polysaccharide complex prepared from several types of soils and from peat (Duff, 1954). As a result of periodate oxidation, two of the sugars were shown to have methoxyl groups attached to the C—2 carbon of the parent sugar.[1] Duff suggested the presence of 2,6- or 2,7-di-O-methylaldopentose, believing these methylated sugars to be of microbial origin because they occur in composted grass but not in fresh grass.

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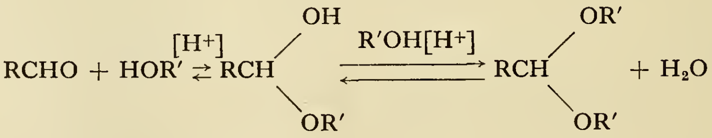
[1] Methylation of sugars proceeds through the formation of sugar acetals or glycosides, i.e. reaction of the aldehyde radical of aldoses with alcohols in the presence of acid catalysts (Noller, 1951, p. 359):



$$RCHO + HOR' \overset{[H^+]}{\rightleftarrows} RCH\begin{matrix}\diagup OH\\ \diagdown OR'\end{matrix} \underset{\longleftarrow}{\xrightarrow{R'OH[H^+]}} RCH\begin{matrix}\diagup OR'\\ \diagdown OR'\end{matrix} + H_2O$$

(hemiacetal) (acetal)

The ring structure of methyl glycosides may be determined by treatment with periodic acid (Malaprade reaction), which cleaves the 1,2-dihydroxy compounds and α-hydroxyaldehydes between the two oxygenated carbon atoms; formaldehyde and formic acid are produced quantitatively.

The methyl glycosides are stable to treatment with alkali and further methylation, in which the remaining hydroxyl groups are converted to ethers, is accomplished

Sugars were found in the A-horizon material of Swiss soils (Duff, 1954) in amounts of 95–100 mg/100 g of organic matter. The substances identified include galactose, glucose, mannose, arabinose, xylose, ribose, rhamnose, and uronic acid. Montmorillonite was found to adsorb these compounds effectively.

Enumeration of carbohydrates found in various natural environments was provided by Vallentyne (after Dubach *et al.*, 1955).

TABLE 5

Sugars in Acid Hydrolyzates of Seston, Gyttja, Peat and Terrestrial Soil (after Vallentyne, 1957)

Source	Sugars
Seston	Glucose, galactose, rhamnose, xylose
Gyttja	Fructose, glucose, galactose, xylose, ribose, arabinose
Peat	Glucose, galactose, fucose, fructose, mannose, rhamnose, xylose, arabinose
Terrestrial soil	Glucose, galactose, mannose, rhamnose, xylose, ribose, arabinose, fucose

Nitrogenous compounds—The *polypeptide–amino acid* content of some humified lake deposits was studied by Blumentals and Swain (1956) and the following amino acids were found to be present in acid hydrolyzates of sediments from several different environments: aspartic acid, glutamic acid, glycine, serine, alanine, threonine, valine, and leucine and/or isoleucine.

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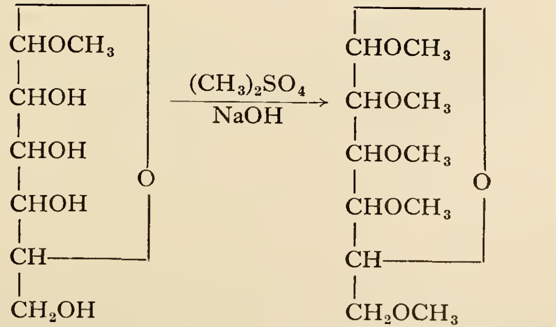
with methyl sulfate in the presence of sodium hydroxide. Methylation of a methy glycoside of an aldohexose is shown below:



methyl glycoside methyl tetramethylglycoside

The same suite was obtained from *humic acid* prepared from Minnesota peat; the amino acids are present either as "impurities" in the humic acid or are involved in the humic acid micelle structure. Free amino acids were not found.

The amino acids obtained from various natural environments were reviewed by Vallentyne (1957), who documents each occurrence with references (Table 6).

TABLE 6

Amino Acids in Hydrolyzates of some Natural Humic Materials (*after Vallentyne*, 1957)

Source	Amino Acids
Seston (plankton)	α-alanine, arginine, aspartic acid, glycine, glutamic acid, histidine, hydroxyproline, leucine, phenylalanine, proline, tryptophan, tyrosine, valine.
Freshwater sediments (peat and gyttja)	α-alanine, arginine, aspartic acid, cystine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, serine, tyrosine, valine.
Terrestrial soil	α-alanine, β-alanine, α-aminobutyric acid, arginine, aspartic acid, cystine(?), cysteic acid, α-diaminopimelic acid, glutamic acid, glycine, histidine, hydroxyproline, isoleucine, leucine, lysine, methionine(?), methionine sulfoxide, proline, phenylalanine, serine, threonine, tyrosine, valine.

Pigments—The study of *chlorophyll degradation products* in humic lake sediments has been carried on by Vallentyne (1957) and others who have reported green pigments in modern and ancient lake sediments. Separation was by chromatography and partial chracterization by absorption spectra, the main absorption peaks in acetone (Vallentyne, 1957, p. 53) being: 411 and 670, 425 and 660, 440 and 662, and 464 and 656 mμ Vallentyne expressed doubt that breakdown of chlorophylls could be accomplished in lake sediments entirely in animal digestive tracts, but the present writer believes this process may affect more of the total sediment than previously considered (Swain and Prokopovich, 1954, p. 1197). The discovery of chlorophyll degradation products in lake deposits 100,000 years old has been reported (Andersen and Gundersen, 1955).

Carotenoids have been found in humus, lakes, marshes, and peats (Vallentyne, 1957, p. 55). The following were reported: α- and β-carotene and xanthophylls (in peats, lakes and marshes); myxoxanthin (lake sediment); rhodoviolascin (pink lake sediment, Kenya); α- and β-carotene (20,000-year-old lake sediments, California); yellow carotenoids (100,000-year-old inter-glacial horizon, Denmark); α- and β-carotene, rhodopurpurin, flavorhodin, torulene, fucoxanthin, petaloxanthin, zeaxanthin or diatoxanthin (= peridinin?), antheroxanthin, glycymerin, leprotene, astacene (?) and other unidentified carotenes.

Hydrocarbons—Hydrocarbons have been found in marine and fresh water humic sediments (Smith, 1954; Swain and Prokopovich, 1954; Swain, 1956). These have for the most part been characterized only as to saturated and aromatic structure by adsorption chromatography. Triacontane, pentatriacontane, and tritriacontane were recognized in peats and marine muds (Vallentyne, 1957, p. 57). Hentriacontane and possibly chrysene, a polycyclic aromatic hydrocarbon, were reported from soils (Vallentyne, 1957, p. 58).

Other organic substances—Information on other substances isolated from lake and ocean sediments and soil was assembled by Vallentyne to whose article the reader is referred for more detailed documentation.

Carbohydrates and related compounds (in addition to those listed in Table 5).
Uronic acids, galacturonic acid and unidentified monomethyluronic acid; in peat hydrolyzate
Methylpentoses; in peat hydrolyzate
Aldobiuronic acid, consisting of glucose bound to glucuronic acid; in water-soluble fraction of soil
Glucosamine; in water-soluble soil fraction
Glucuronic acid; in water-soluble soil fraction
Monomethylhexose, probably methylglucose and methylgalactose; in hydrolyzates of soils
Galactosamine; in soil hydrolyzate
Mannitol; in soil
Heterocyclic N-C-N compounds (purines, pyrimidine, nucleic acids)
  Dinucleotides: guanine-cystosine dinucleotide and adenine-uracil dinucleotide; in peat
  Purines, undifferentiated; in lake muds and peat
  Pyrimidines, undifferentiated; in peat
  Purines: xanthine, hypoxanthine, adenine, guanine; in 2% NaOH extracts of soils
  Pyrimidine: cytosine; in 2% NaOH extract
Miscellaneous nitrogen compounds
  α-Picoline-γ-carboxylic acid; from Hawaiian soil in crystalline form
  Cyanuric acid; from soil
  Choline; from soil
  Creatinine; from soil
  Allantoin; from soil
  Auxins; in aquatic sediment and in soil
Fats, Waxes, Non-Nitrogenous Acids and Alcohols
  Fatty acids ranging from C_6 to C_{30} resembling caproic ($C_6H_{12}O_2$), heptoic ($C_7H_{14}O_2$), caprylic ($C_8H_{16}O_2$), pentacosanoic ($C_{25}H_{50}O_2$),

heptacosanoic ($C_{27}H_{54}O_2$), cerotic ($C_{26}H_{52}O_2$), montanic ($C_{28}H_{56}O_2$) behenic ($C_{22}H_{44}O_2$), and arachidic ($C_{20}H_{40}O_2$) acids, from peat wax; caproic acid, cerotic acid, melissic acid ($C_{30}H_{60}O_2$) and possibly montanic acid; from marine sediments.

Alcohols; from peat wax, an unidentified alcohol, heptacosanol ($C_{27}H_{56}O$), and Vaseline-like mixtures; soil lipids: glycerol ($CH_2OHCHOHCH_2OH$)

Free organic acids; lake sediments: formic ($HCOOH$), acetic (CH_3COOH) and butyric ($CH_3CH_2CH_2COOH$) acids; more than a dozen free acids have been isolated from soil

Inositol ($C_6H_6(OH)_6$), in soil as inositol-hexaphosphate, etc.

Aldehydes: salicylic aldehyde (HOC_6H_4CHO), trithiobenzaldehyde ($S_3C_7H_5CHO$), and vanillin ($CH_3O(OH)C_6H_3CHO$) have been obtained from soils

Vitamins

Vitamin A: in soil

Thiamin (B_1); in pond mud and in soil

Riboflavin (B_2); in soils

Vitamin B_{12}: in salt marsh concentrations, in pond mud and in soil extracts

Biotin (H): in soil, with quantities decreasing with depth; *Sphagnum* peat, diatom-rich plankton, and forest humus are believed to be richer sources of biotin than cultivated or pasture soils.

Pyridoxine ($C_8H_{11}NO_3$): in soil

p-aminobenzoic acid ($NH_2C_6H_4COOH$): in soil

Other substances

Ultraviolet fluorescing substances of four types, characterized by absorption spectra; in extracts of marine sediments and gyttja

Opalescent liquid, ether-soluble, possibly a thio-derivative of an unsaturated aliphatic hydrocarbon; in Black Sea sediment

Partly crystalline lipoid; in beach mud.

Enzymes: catalases, peroxidases, and proteolytic enzymes in river and marine muds; urease-like ammonia-forming dephosphorylating, and deaminating enzymes in soils.

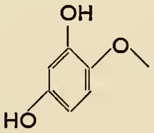
Humic Acids

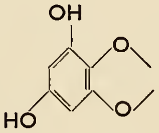
The chemical constitution of humic acids as it was understood up to 1938 was exhaustively reviewed by Waksman (1938). A long series of terms have been introduced for humic acid-like substances. *Ulmin* referred to dark material extractable with alkali from elm trees (Ulmus); later the term was applied to alkaline extracts of coal; *terreau* is the dark-colored material formed on decaying plants in moist air; *humus acid* was used by Dobereiner in 1822 for the dark-colored fraction of soil organic matter, and Weigmann, in 1837, used "humic acid". Important early work on the properties of humic acid was done by Sprengel around 1826. *Humates* are substances precipitated by salts of alkali earths and heavy metals except gold; "mylla" and "geic acid" were used as synonyms of humic acid by Berzelius, who also used "mull coal" as a synonym of humin; *crenic acid* was prepared by Berzelius by extracting humic material with hot potassium hydroxide, saturating the solution with acetic acid and adding copper acetate, whereupon a brown precipitate, "copper apocrenate", formed. After the remaining free acetic acid was neutralized with ammonium carbonate, a grayish green "copper crenate" precipitate formed. Decomposition of the copper compounds with hydrogen sulfide brought free "crenic acid" into solution; oxidation produced "apocrenic acid". The latter was found to be partly soluble in water and alcohol, was dark colored, formed insoluble compounds with silicic acid and with aluminum hydroxide, could be precipitated with inorganic acids, and was otherwise closely similar to humic acid. Various names were applied to humic acid preparations from various sources, i.e., glucic acid (from glucose), torfic acid (from peat), acet-ultic acid (from a mixture of acetone and chloroform), xylyl acids (from rotting wood), fumic acid (from stable manure), sacculmic acid (from sucrose), melanoic acid (from proteins), fulvic acid, hymatomelanic acid, pyrohymatomelanic acid (phenol-soluble fraction of humic acid), and humal acid (water soluble).

Definition—A recent article by Thiele and Kettner (1953) has provided a valuable review on humic acids.

Humic acids may be defined as "polymeric colloidal substances composed of polymeric bodies (polyonen), which are in turn composed of monomeric bodies (mononen). The monomeric bodies are considered to be made up of units of the following structural elements: (1) a nucleus, (2) a bridge element and (3) a reactive group.

The nucleus is believed to be a C_6 ring, the "bridge" element may be —O—, and the reactive group may be OH, as in the following examples:





Optional groups may occur as follows: the *nucleus* can consist of simple five- or six-membered rings or of condensed rings, for example: benzene, naphthalene, anthracene, pyrrole, thiophene, pyridine, indole, or cyclic benzene-like compounds. The *bridges* bind the "building blocks" together and can consist of —O—, —NH—, —CH_2—, or —S—. The *reactive groups*, hydroxyls, are important in that they provide the acidity, the hydrophilic properties, base-exchange capacity and the tannin-like character.

Humic acids may be further defined as "polymeric polyphenols of benzene-like ring systems"; hymatomelanic acids and fulvic acids also have this definition, but the degree of polymerization is in the following order:

Humic acid > hymatomelanic acid > fulvic acid.

Preparation and separation—Humic acids are prepared by extracting naturally occurring humus substances with one of the following media: NaOH, LiOH, NH_4OH, Li_2CO_3, or Na_2CO_3. The concentrations of these media have been varied from 0.5 N to dry digestion, and the time of extraction may proceed for several weeks. As the reaction time continues, however, the humic acids change to a lower degree of polymerization and fade in color. Extraction with NaF resulted in "pure" humic acids but in smaller amount, because acid bound to Al or Fe salts is not extracted; only those acids bound to Ca salts. Sodium tetrapyrophosphate is reported to give good yields. The extracted humic acid is precipitated with hydrochloric or dilute sulfuric acid.

Methods for the separation of artificial "humic acids" from various substances by condensation, dispersion, and permutoid conversion have been worked out.

1. *Condensation.* Formation of humic acids by: oxidation of phenols and polyphenols in alkaline solution, or of aromatic amines; building up of molecularly dispersed carbohydrates in acid solution through dehydration and cyclization; building up of sugars with amino acids (melanoidins) through dehydration and condensation; condensation of phenols and polyphenols with formaldehyde and with methylene groups as the bridges.

2. *Dispersion.* Formation of humic acids from graphitic acid by making a suspension of it sufficiently alkaline with KOH to prevent coagulation, or adding a few ml of 30% H_2O_2 and allowing to stand; from Acheson-graphite of 99.99% purity and 100 μ size slurried with $K_2S_2O_8$ and with 2N NaOH, after which the mixture is covered with additional NaOH. The humic acid thus formed diffuses into overlying clear NaOH solution, which is decanted and collected.

3. *Topochemical or permutoid reaction.* From artificial resin cation exchanger by grinding and repeated extraction with NaOH; from "Willstätter Lignin", finely pulverized by first removing humic acids already formed during preparation of lignin, followed by treatment with 2N NaOH and 30% H_2O_2 (0.5 ml/g of lignin); humic acid from cork can be prepared in the same way. Collection and purification is by means of centrifugation.

Reactions and properties—*Coalification* is said to result from heating of alkali-soluble humic acid to produce alkali-insoluble brown-coal-like substance. Artificial "coalification" of a carbohydrate was effected by gradual removal of water with concentrated sulfuric acid, phosphoric acid, or zinc chloride; the following sequence of events was suggested: glucose → fulvic acid → hymatomelanic acid → humic acid → humin → amorphous carbons. The latter show none of the interference rings of graphite in Debye–Scherrer X-ray photographs. This process of slowly condensing glucose to "humic" substances finds a parallel reaction in the formation of *melanoidin* by condensation of glucose and glycine. If the dehydration reagents (H_2SO_4, etc.) are dilute and the temperature low, a long time is required for the process.

The formation of "humic acid" under biological conditions through the oxidation of polyphenols (pyrogallol, hydroquinone, resorcinol, guaiacol, etc.) has been accomplished in the presence of phenoloxidase (enzyme). The process is one of condensation. It is not known which specific enzymes affect condensation, and which degradation, of humic acids.

The elementary *chemical composition* of humic substances was studied by Thiele and Kettner, who from a series of preparations made under the same conditions in their laboratory, reported the following:

TABLE 7

Composition of Humic Preparations (after Thiele and Kettner)

Preparation	Carbon (per cent)	Hydrogen (per cent)	Oxygen (per cent)
Phenol-formaldehyde	68.35	5.68	25.97
Phenol-formaldehyde, strongly condensed	70.30	5.80	23.90
Resorcinol-formaldehyde	64.77	4.69	30.54
Pyrogallol-formaldehyde	57.16	4.07	38.17
Hymatomelanic acid	55.08	4.50	40.42
Glucose "humic acid"	60.94	4.67	34.39
Humin I	61.06	4.62	34.32
Humin II	61.86	4.50	33.64
Melanoidinic acid	58.39	5.23	32.78
Melanoidin	66.02	5.55	26.93
Nigrosin	62.48	4.07	25.05

Attempts to characterize various humic acids by means of *electrometric titration* have not been successful; inflection points from which the equivalent weight of humic acid could be calculated were not obtained; instead the electrotitration curves were reported to resemble adsorption isotherms of colloidal substances. Recently Pommer and Breger (1960, 1960a) re-interpreted Thiele and Kettner's curves and demonstrated them to be titration rather than adsorption curves. The equivalent weight of humic acid was found to be about 150, and the phenol–formaldehyde and pyrogallol–formaldehyde resins were not found to be true analogues for natural humic acid.

The *cation exchange capacity* of various humus substances varies over a considerable range and permits conclusions as to the number of exchangeable hydrogen ions and the equivalent weight. Carbon dioxide must be excluded from the system, and at best the determinations are only semiquantitative. The exchange capacity of undried humus substances expressed in mg of $BaSO_4$ per 100 g and milliequivalents per 100 g are as follows (after Thiele and Kettner):

TABLE 8

Exchange Capacity of Humus Substances

Humus Substance	Mg $BaSO_4$	Meq/100 g
Humic acid (Merck)	291.0	250
Humic acid from glucose	295.1	253
Humin I	152.7	131
Humin II	139.8	120
Melanoidin	125.9	108
Aniline black	0	0
Nigrosin (alcohol soluble)	0	0

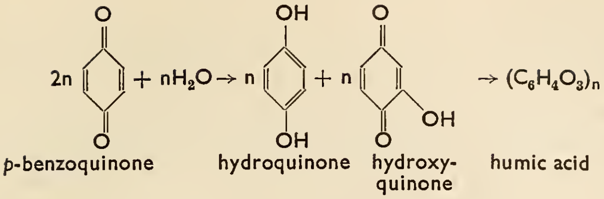
Drying decreases the ion exchange capacity, and further humification and coalification likewise cause a decrease in exchange capacity.

When the humic substances were subjected to *electrophoresis* it was found that the humic acids, except those containing nitrogen, migrate to the anode and are, therefore, considered to be colloidal anions. Humic bases and nitrogenous humus substances tend to migrate to the cathode but quickly precipitate. It was also found that separations of humic substances were possible by means of *paper chromatography* followed by electrophoretic application of 3 to 20 mA at 220 or 400 V. Individual humic acids, fulvic and hymatomelanic acids, and nitrogen-bearing samples are reported to be separable; the latter show darker colors on the chromatogram.

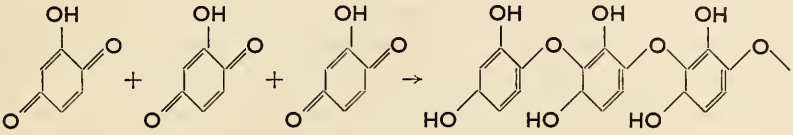
The X-ray investigation of humic acids shows no interference rings and the material is assumed to be amorphous. Preparations of humic acids from graphitic acid or graphite, however, still retain the X-ray patterns of graphite.

Constitution—A comprehensive discussion of the possible chemical constitution of humic acid is given by Thiele and Kettner. The theories of Eller and of Erdtman which hold to a dimeric or polymeric hydroxyquinone origin as held by Fischer and Schröder; the condensed phenolic quinoid, etc., nuclear ring origin as proposed by Fuchs and by Schultze and Flaig; and the concept of Marcusson of condensation of two molecules of furfural to a "peridifuran" ring—all these theories are considered to be unsatisfactory by Thiele and Kettner.

The benzenoid origin of humic acids as proposed by Laatsch (1944) is thought to be a plausible one. In the decomposition of p-benzoquinone in the absence of an oxidizing agent, half is converted into humic acid and the other half to hydroquinone. The latter results through disproportionation accompanied by absorption of two hydrogen atoms; the oxygen freed in the process must react with the quinone leading to re-establishment of hydroquinone, thence to formation of humic acids without further addition of oxygen.

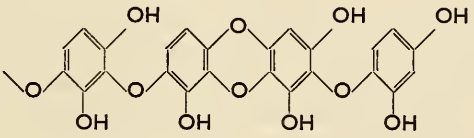


The polymerization of the hydroxyquinones to a benzenoid system may proceed as follows:



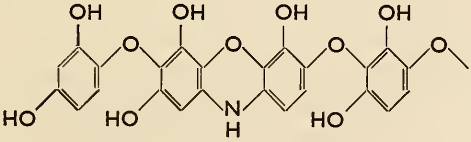
If a molecular weight of about 1200 be assumed, ten hydroxyquinones form a colloidal micelle of humic acid.

This $C_6H_4O_3$ monomer, although believed to be stable, could further be oxidized with development of double oxygen bridges between some of the benzenoid rings:



Additional oxidation beyond that in the bridging phenomenon results in oxidative splitting of the quinoid rings; additional oxygen may become available during humification if more hydroquinone than humic acid is formed from the hydroxyquinone.

The form in which nitrogen occurs in humic acids is problematical, but it may be incorporated in the humic acid molecule as a bridge substance of the nature of oxazine:



The presence of nitrogen results in a decrease in the acidity, allows more oxygen to be taken up, and in turn provides a greater stability of the nitrogenous molecules.

Erdtman (1943, p. 14) emphasized that the coloring matter must play some role in the structure of humic acids. When brown acids are treated with sodium amalgam in the absence of air, the color is lost or fades greatly owing to formation of sodium salts of leucohumic acids; on exposure to air, the solution absorbs oxygen and the color reappears. A quinoid nature of humic acids is thereby indicated. Further evidence of quinoid structure is found when humic acids are treated with acetic anhydride and zinc dust to form feebly colored stable leucoacetates. These may be hydrolyzed to leucohumic acids and, if oxygen is available, to humic acids.

A suggestion by Mukherjee and Lahiri (1956) that humic acid molecules involve a flexible linear structure analogous to that of a linear polyelectrolyte such as Krilium, was based on observed reduction in viscosity of humic acid solutions with increase in solute concentration. They believe that polynuclear condensed aromatic structure, commonly assigned to humic acids, would not be able to undergo changes in configuration implied by the changes in viscosity they observed. Srivastava and Berkowitz (1960) found that flexible linear polyelectrolytes, both coiled and uncoiled, degrade readily when submitted to sonic and ultrasonic fields, but that humic acid preparations do not. They suggest, alternatively, that a permissible structure for humic acids is that of small (3 to 4 ring) condensed aromatic areas linked by double methylene bridges.

Amino acids and other nitrogenous materials in humic acid—Several investigators have found humic acids to contain amino acids (Okuda and Hori, 1954). Humic acids were prepared by extracting loam or humic clay loams with 0.15 M sodium pyrophosphate, neutralizing with concentrated H_3PO_4, filtering, centrifuging, acidifying, recentrifuging and washing. The preparation was hydrolyzed with 6N HCl and, after removal of excess acid, the hydrolyzate was chromatogrammed on paper to yield the following amino acids:

arginine
lysine
histidine
phenylalanine
serine
threonine
leucine
valine
glutamic acid
aspartic acid
glycine
alanine
proline

Lignins prepared from rice and wheat straws, pine needles, and oak and cedar leaves also were hydrolyzed with hydrochloric acid. Chromatograms of all the samples, except that from rice straw, showed the presence of all the above amino acids together with tyrosine. Rice-straw lignin also contained methionine. No free amino acid was found in any of the preparations. In a later paper, these authors (Okuda and Hori, 1956) reported the same groups of 13 amino acids from humic acid hydrolyzates of four different soils together with tyrosine and cystine.

A group of 8 or 9 amino acids was found in HCl-hydrolyzates of humic acid from Minnesota peat by Blumentals and Swain (1956). The humic acid was prepared by sodium hydroxide extraction of the peat followed by precipitation with hydrochloric acid, filtering, and centrifuging. The following were obtained: aspartic acid, glutamic acid, glycine, serine, alanine, threonine, valine, and leucine and/or isoleucine. This suite of amino acids is the same as that obtained from lake sediments in Minnesota.

The amino acids, total nitrogen, amino nitrogen, and nonhydrolyzable nitrogen were determined in "A-type" humic acid by Hayashi and Nagai (1953) from several soils. Fifteen amino acids were detected from humic volcanic ash soil and low moor soils, while from black soil, high moor peat, and rice-straw lignin, 14 amino acids were obtained. Sulfur was not found in these amino acids.

Studies of the nitrogen in humic acids obtained by various methods of extraction were made by Rydalenskoya (1951). A neutral solvent (1% NaF) was found to dissolve no humic acid from terra rosa, and up to 68% of humic acid in humus-alluvial soils; the remainder of the humic acids could be dissolved by 0.1 N sodium hydroxide. If the sample had been previously decalcified by sulfuric acid, extraction of all the humic acid was accomplished with the sodium hydroxide (the sulfuric acid would also have extracted some humic acid). Similar results were obtained by Souci and Gels (1941). The two extracts are believed to be chemically homologous. The nitrogen content was found to be much higher in the sodium hydroxide extract than in the sodium fluoride extract, but hydrochloric acid hydrolysis of the former brings its nitrogen content down to the level of the latter. The nitrogen is believed to be present in the humic acid extracts in the form of polypeptides rather than being part of the humic acid "molecules".

The amino acid content of humic acids from *Streptomyces* has been studied by Bremner, Flaig, and Küster (1955). It was found that a hydrolyzate of this type of humic acid contains about 10 times as much tyrosine as do humic acids from soil. On the other hand, the soil humic acids contained the following amino acids not present in streptomycetic humic acid: hydroxyproline, α-aminobutyric acid, methionine sulfoxide, methionine sulfone, and α-e-diaminopimelic acid.

A comparison has been made between the non-precipitable "B(rown)" and precipitable "G(ray)" humic acid fractions of black earth in regard to their contents of amino acid and nitrogen (Bremner, 1955). There was no marked difference in the total amino acid composition of the two fractions as determined by paper chromatography, however, the B fraction contained a higher proportion of its nitrogen in the form of acid soluble and α-amino nitrogen than did the G fraction.

An investigation of the amino acids in hydrolyzates of humic acids from different soils was made by means of paper partition chromatography (Panel, Kalousek, and Smatlak, 1954). The soils were of the chernozem, brown, and podzolic varieties. The following amino acids were separated: cysteic, aspartic, glutamic, dihydroxyphenylalanine, serine, glycine, threonine, α-alanine, lysine, arginine, proline, valine, methionine, methionine sulfone, tyrosine (trace), and two unidentified substances. It is believed by the authors that the organic sulfur of the humic acids is a structural element of cysteic acid and methionine. These amino acids are stated to show polypeptide chain structure indicating their proteinaceous nature in the humic acids.

The nitrogen content of Russian peat humic acid was 1.72% before hydrochloric acid hydrolysis, and 0.97% after hydrolysis; from a chernozem the nitrogen content was 4.04% and 2.65%; and from a podsol, 4.86% and 1.79%, respectively (Dragunov, 1950). It was stated that the monoamino acid content made up 64–75% of the total nitrogen in the hydrolyzates.

It was found that when humic acid (250 mg.) was added to a 250 ml solution containing 0.05 mg of alanine, aspartic acid, and glutamic acid and the mixture exposed to sunlight under aseptic conditions, ammonia was produced. The yields of NH_3 in mg/l. after 120 hours were: 64.21, 42.34, and 42.42, respectively. Humic acid was, therefore, viewed as having photocatalytic properties. Keeping in mind the content of amino acid nitrogen and other nitrogen in the humic acid, the validity of this experiment might be questioned.

Early experiments on the nitrogenous contents of humic acids were performed by Dragunov and Bakhtina (1934). They found that "humic acid protein" is hydrolyzed to amino acids by heating with water. A sedge-moss peat yielding 47% humic acid contained 2.31% nitrogen of which 50–60% could be hydrolyzed to amino acids; lowmoor sedge peat yielded 53% humic acid containing 2.03% nitrogen of which 13–22% was hydrolyzable; corresponding values for buried lowmoor peat were 31%, 3.2%, and 20%, respectively. It was further found not only that amino acids are readily separable from humic acids, but that the remaining nitrogen is partly NH_3 and partly in a form unaffected by treatment with acid or alkali. As the humic acid content of peat increases, the amount of hydrolyzable nitrogen decreases, suggesting that nitrogen is gradually acquired as an amine bridge during humification.

Charmbury and collaborators (1945) found that the nitrogen in "regenerated humic acids" obtained from nitric acid extracts of bituminous coal occurs in two different forms: (1) the major portion can be liberated as the nitrate ion upon $KMnO_4$-oxidation and is in a highly oxidized state; (2) the smaller portion is liberated as ammonia both by alkaline $KMnO_4$ and by boiling alkali, and is in a less oxidized state. After comparison of the highly oxidized nitrogen with known compounds, including p-aminobenzoic acid, p-nitrobenzoic acid, α-benzoinoxime, and α-nitroso-β-naphthol under various conditions, the authors decided this nitrogen-fraction must be in the form of —NO_2 groups. The less oxidized nitrogen, they believe, is at the nitroso (ON) or the isonitroso (HON) level.

Carbohydrates in humic acid—Although carbohydrates undoubtedly are of common occurrence in humic and fulvic acids, there are few published investigations on this subject. According to P. Dubach and D. L. Lynch (unpublished ms., Dept. of Biochemistry, University of Minnesota) fulvic acid fractions of soil extracts they studied contain considerable quantities of pentoses, as shown on paper chromatograms of their hydrolyzates. Arabinose was commonly found. Uronic acids are found associated with soil humic acids, and Dubach and Lynch found uronic acids to be roughly correlative with total organic carbon in their soil samples.

Some Recent Investigations of Humus Deposits

Soil humus—A systematic study of soil humus in forest floors of Saskatchewan was made by Gross (1946). Three types of forest-floor soils were recognized: granular mor, dry mor, and matted mor. The granular and dry mor types are more acid than the matted mor; mineral content is higher in the dry and matted mor than in the granular mor; under deciduous trees the mineral content is higher than under conifers; nitrogen content of humus in dry mor is lower than in granular or matted mor; the nitrogen in the matted and granular mor is mainly tied up in the lignin fraction, whereas that in the granular mor is about 25% of hydrolyzable, proteinaceous nature; and carbon/nitrogen ratios of the humus in granular and dry mor were higher than in matted mor. A decrease in ether-soluble materials accompanies decomposition of the leaf litter, and a slightly acid nature of these materials in granular mor was observed, probably due to phenolic compounds. Hemicellulose increases with progressive decomposition of the leaf litter whereas it decreases in the other mor types. Cellulose decreases rapidly and lignin increases in all forest types with decomposition of the leaf litter; shallow peats are similar to forest floors in composition, and *Sphagnum* peat is characterized by high content of hemicelluloses.

The reactions occurring between humic acid and sodium humate in contact with Ascarite, kaolinite, podzol and chernozem soils have been described by Aleksandrova (1954). Exchangeable calcium ions enter into reactions with the humic acids, and iron oxides plus aluminum oxides form combinations with humic acids giving rise to gelatinous membranes.

Peat humus—Procedures for treatment of peat to yield products of possible commercial interest were outlined by Christiansson (1946, 1947): (1) low-temperature carbonization to yield products consisting of furan (5%), 2-methylfuran (25%) and probably 2,5-dimethylfuran (5%); (2) extraction with organic solvents giving waxes, resins, and, at elevated temperatures and pressures, products useful for hydrogenation; (3) hydrolysis of peat with mineral acids under pressure yielding furfural, sugar, and a residue which can be freed from water by pressure; (4) hydrogenation to oils; (5) controlled oxidation to organic acids; and (6) gasification. Pentane and isopentane also were obtained in (1).

A study of the progressive decomposition in New Zealand peats led Bailey (1953) to the conclusion that, whereas the near-surface decomposition of carbohydrates is mainly bacterial, the formation of humic acids continues to greater depths and is probably a chemical process.

A recent investigation of 13 Russian peat samples gave the following results (Zhuraoleva, 1954): surface portions of peats have high bitumen and carbohydrate content and relatively low lignin and humic acid. As decomposition progresses in these peats, bitumen and hydrocarbons increase and carbohydrate decreases. Deeper parts of peat have low bitumens and cellulose, and are relatively high in lignin and humic acid.

According to Titov (1953), the difference in the composition of the top and bottom peat layers is mainly the result of differences in the salt contents of the bog waters. In alkaline bog waters there is a tendency toward mechanically weak peats, with ash relatively high in lime, low hydrogen content, and low bitumens; calcium humates are prominent in such peats. The peats formed in soft waters are low in ash and produce mechanically strong briquettes. The author suggests a relationship of these features to the formation of earthy brown coals.

Water humus—Waters containing humic acids and iron compounds may be purified of the iron by use of flocculating agents (lime, etc.) or by chemicals which destroy the organic matter ($KMnO_4$, etc.) (Reckmann, 1934). This process may be effective in the accumulation of bog iron ore in marly ponds or in water containing free sulfuric acid.

Sapropelic accumulations in lakes are considered to represent in large part accumulations of humic materials rather than to consist simply of settled plankton (Kazakov, 1950). It is probably more nearly correct to visualize these accumulations as comprising settled plankton in various stages of aerobic and anaerobic humification.

The humic accumulations of two lakes in Russia were compared by Goryunova (1954). Glubokoe Lake is rich in humic material drawn from surrounding swamps, whereas Beloe Lake contains abundant humates originating through the activity of plankton and man. Neither simple sugars nor maltose were detected in either lake. Beloe Lake is low in starch, the cellulosic material that occurs near the surface is absent at depth. Saturated fatty acids of high molecular weight are present, and the bulk of the organic matter in solution was thought to consist of polysaccharides.

Sapropels from the Ural mountain region were found to contain bitumens, water-soluble substances, hemicelluloses, pentosans, methylpentosans, uronic acids, cellulose, humic acids, humins and non-hydrolyzable residue (Ponomarev, 1947). Humic acids and "humins" were found to comprise 52–55% of the organic matter, with the filtrate from the acid precipitation of humic acids in the 1% NaOH extract predominating. Hemicelluloses forming 9.3–13.8% of the organic matter are about one-half pentosans. The author recognized two types of sapropel: (1) a siliceous type with high content of bitumens (7%), carbohydrates (17.6%) and nitrogen (4.7%); and (2) a calcareous type with low bitumens, carbohydrates and nitrogen and a high content of nonacid humins.

Humic materials in rocks—There has been a great deal of research on the bitumen content of rocks, particularly on that of the oil shales from which various hydrocarbons can be obtained by distillation or hydrogenation. The "pyrobitumen" fraction of the organic matter has been studied only slightly (see Chapter 8).

The light brown to black organic substance of oil shales and other rocks, insoluble in petroleum solvents, but yielding oils on distillation has been called "kerogen". Kerogen from the Eocene Green River Oil Shale of Colorado, Utah, and Wyoming occurs as an impregnation of the calcite-dolomite "marlstones" of that formation. The kerogen consists physically of amorphous yellowish, reddish brown, and black organic material together with up to 50% of mascerated organic debris of plants, algae, spores, pollen, insect parts, etc. Chemically it contains: carbon, 69–80%; hydrogen, 7–11%; nitrogen, 1.25–2.5%; sulfur, 1–8%; oxygen, 9–17% (Levorsen, 1954, p. 28). A comparison of atomic H/C ratios for kerogen obtained from several sedimentary formations with those for asphalts and coal was made by Hunt and Jamieson (1956, p. 483):

TABLE 9

Hydrogen/Carbon Ratios for Asphalts, Kerogen and Coals

Substance	Atomic H/C Ratios
Asphalt extracts of shales	1.30–1.64
Natural asphalts	1.24–1.60
Kerogen from shales and dolomite	0.68–0.90
Lignite	0.7–1.0
Bituminous coal	0.5–0.7

Kerogen is believed to be related to the cannel coal series in that with increasing amounts of cutinaceous, waxy and resinous substances the material passes from kerogen to torbanite, boghead coal, and finally to cannel coal (Down and Himus, 1940; Schopf, 1949).

Kerogen-bearing oil shales are widespread, but are best known in Scotland, Sweden, Russia, Manchuria and the United States. The yield of the oil shales from various localities is as shown in Table 10. (Tiratsoo, 1951, p. 297).

Materials related to kerogen include: dopplerite, see above; tasmanite, sandy shale rich in spores; sulfur rain, recent accumulations of pollen; leuchttorf-torch peat, solidified spore and pollen accumulation; torbanite-boghead coal, gelatinous accumulations of the algae *Reinschia*, *Pila*, and *Botryococcus*; kukersite, oil shale rich in alga *Gloexapsamorpha prisca* remains; coorongite, rubbery accumulations of *Elaeophyton* algae; n'hangellite, green elastic accumulations of the alga cf. *Coelosphaerium*; and various liptobioliths (Stutzer and Noe, 1940, p. 118).

The tar from the Scottish oil shales is a black liquid with greenish fluorescence, containing 80–90% of paraffins and some cresols and phenols.

TABLE 10

Yields of Shale Oil and Ammonium Sulphate from Various Shales

Locality and geologic horizon	Shale oil gal/ton	Ammonium sulfate lb/ton
Scotland (Lothian)	10–55	6–70
England (Kimmeridgian)	10–40	10–50
N.S. Wales (Coorangite)	14–150	20–30
New Brunswick (Albert)	30–51	67–111
Nova Scotia (Acadian)	4–23	9–40
Eastern U.S. (Chattanooga)	4–45	0–10
Utah (Green River)	6–10	40–50
Colorado and Wyoming (Green River)	10–68	22–34
Esthonia (Kukersite, Silurian)	70–80	5–15

These oil shales are of Carboniferous age and are found as nearshore bituminous shale of the upper Dinantian (Visean) Series (Gignoux, 1955, p. 176).

The oil shales of Colorado, Utah, and Wyoming are of lacustrine origin occurring in the Eocene Green River formation (Bradley, 1929). In their study of the organic compounds of these oil shales, Hunt, Stewart, and Dickey (1954, p. 1692) recognized an environmental control of the distribution of the kerogen-bearing beds. The Eocene lakes went through an early low-salinity condition in which paraffinic and condensed-ring aromatic compounds were prominent, and a later high-salinity stage in which aromatics and nitrogenous compounds and finally naphthenes were abundant. In the later Green River and Uinta Epochs of the Colorado–Utah Eocene, pyrobituminens of low oxygen content, such as wurtzilite, ingramite and albertite can be recognized in the kerogen-bearing deposits. These have characteristic infrared absorption spectra (see Chapter 8).

A sample of the Green River oil shale from a deep well core was treated with hydrochloric acid at the University of Minnesota and the distillate from it gave a positive test for furfural (J. G. Palacas, personal communication). The solution absorbed in the 280–285 mμ range, indicating furfural and hydroxymethylfurfural. A sulfuric acid hydrolyzate of this oil shale was chromatographed on Whatman No. 1 filter paper in butanol/acetic acid/water, and the chromatogram sprayed with aniline and phthalic acid. A substance of the nature of humic acid developed on the chromatogram. Humic acid from Minnesota peat was co-chromatogramed. Both absorb strongly at 264.2, 268 and 271 mμ, suggesting a pyridine compound.

The bitumen of the Gdorsk shale, studied by Karavaev and Vener (1953), was found to be a high-molecular weight material with phenolic, ketonic, and pyridine groupings. Upon treatment of the bitumens with anhydrous $AlCl_3$, alkali-soluble products containing phenols were obtained. Hydrolysis of the bitumen with sulfuric acid and hydrochloric acid was accompanied by the formation of phenols having the average composition $C_{10}H_{14}O$. Oxidation of the bitumen with $KMnO_4$ yielded fatty acids but no benzenecarboxylic acids. The lack of water formed from the large number of hydroxyl groups during pyrolysis of the bitumen was considered to be evidence for the absence of carbinol groups. Pyridines were formed with the phenols during acid hydrolysis, and this was believed to justify the suggestion that pyridine- as well as phenol-type groups were present in the shale. The oxygen apparently occurs in forms other than carboxyl, carbonyl, and hydroxyl.

Humic acids and related substances have been obtained by alkaline extraction of carbonaceous shales. *Dictyonema* (graptolite) shales could be divided into three types based on their organic matter (Uspenskii, 1938): (1) a type containing 10.74–23% organic matter of which 0–4% was humic acid; (2) a type containing 6.45–11.13% organic matter, of which 50–90% was humic acid; and (3) a type in which there was 5.85–17.76% organic matter containing 10–40% humic acid. There were also differences in moisture, sulfur, and ash content. The C/N ratios were 15–17.

Substances similar to humic acid were obtained (Khristeva, 1938) from carbonaceous shale by extraction with KOH and KNO_3 (4 : 1 ratio) at 270–300°C. The phosphorus present in the shale was extracted with the humic acids, and is thought to have been in combination with the organic substances.

Organic matter associated with Arkansas bauxite was found to account for 0.3–4% of the rock (Utley, 1938). The humic acids extracted from the organic matter contained 52–56% carbon; nitrogen and sulfur were also present. The low carbon content of these humic acids, compared to those from lignites, suggest that combinations as humates occur in the bauxite. The humic material is believed to have been derived mainly from the lignites which overlie the bauxites. The ash from the lignites was predominantly aluminum silicate and Al_2O_3, whereas that from the bauxites is mainly Al_2O_3.

A proposal has been made that humic acids produced in swamps such as the Okefenokee, may be converted to asphalts and eventually to crude oil (Haseman, 1921, 1930; Corbett, 1955). The chemical changes necessary to consumate this phenomenon have not been adequately described.

Mineral Concentrations Related to Humic Materials

Humus solutions are effective in the transportation and subsequent concentration of a variety of mineral substances, as bog ores, nodules in marine strata, etc. In addition, many elements are concentrated by organisms and may be extracted from their tissues or body fluids, detected in ash preparations of them, or used by them in skeletal construction.

It is well known that *iron* and *silica* are transported in waters rich in organic matter, evidently as stable humic complexes. The humic materials are in the form of "protective" colloids which inhibit flocculation and precipitation of the iron and silica by electrolytes (Gruner, 1922, p. 459; Rankama and Sahama, 1949, p. 554, 665). The iron, silica, calcium oxide, and magnesium oxide which could be dissolved from various minerals and rocks in peat solutions was determined by Gruner (1921, p. 427); results are summarized below:

Table 11

Solubility of Minerals and Rocks in Peat Solutions in ppm (after Gruner, 1922)

Minerals	SiO_2	Fe	SiO_2	Fe	CaO	MgO
	After 77 days		After 182 days			
blank	1	tr	6	2	9	tr
pyrite	nd	23	9	14	7	tr
hematite	tr	25	10	27	8	tr
limonite	tr	14	15	30	7	tr
magnetite	nd	31	8	41	10	tr
siderite	tr	94	10	48	9	tr
Rocks	After 90 days		After 165 days			
augite	40	9	35	8	31	2
olivine	161	14	106	9.5	8	24
greenstone	81	20	68	15	16	tr
Duluth gabbro	78	19	82	15	16	tr
Greenalite rock	47	17	44	9	8	2
Magnetic iron chert	30	27	33	25	14	2
Glauconitic sand	26	15	35	19	29	3
Sudbury ore	25	22	30	16	44	tr

In the absence of oxygen and with only small amounts of dissolved organic matter, ferrous iron may be taken directly into solution from the rocks as iron bicarbonate, $Fe(HCO_3)_2$, (Rankama and Sahama, 1949, p. 663); precipitations occur as siderite, $FeCO_3$, when carbon dioxide is removed from the solution. On the other hand, if humic matter is abundantly dissolved in the water, and oxygen is present, iron is taken up as iron hydroxide (Gruner, 1922, p. 445), carried adsorbed to organic colloids, not as bicarbonate, and incompletely precipitated as hydroxide.

If iron is present in an adsorbed condition in deoxygenated waters, addition of sulfates of alkalies or alkaline earths or their carbonates, i.e., neutralization, will cause precipitation of the iron as sulfide (Gruner, 1922, p. 445). In the presence of air, iron hydroxides will form instead.

A certain amount of *magnesium* may accompany iron if the latter moves in solution as bicarbonate as a result of oxidation of associated organic matter (Rankama and Sahama 1949, p. 456). Deposition of ferromagnesite, $(Mg, Fe) CO_3$, or ankerite may result. The latter mineral is rather common in unweathered sedimentary rocks.

Silica in solution as a colloid is easily precipitated by electrolytes and by colloids with an opposite charge. In solutions that contain protective organic colloids silica is more stable; electrolytes are ineffective precipitants; algae, Radiolaria and diatoms, however, bring about the deposition of silica (Gruner, 1922, p. 457); see Chapter 14.

The presence of humic substances in waters participating in the chemical weathering of *aluminum* bearing rocks will remove iron and leave behind pure kaolinite or other high-alumina clays (Noll, 1935). *Beryllium* may be concentrated in a similar way. The fact that aluminum is soluble in acid (pH 4) or in basic (pH 7–9) solutions but is precipitated as $Al(OH)_3$ in intermediate pH ranges probably rules out humic solutions as transporters of aluminum. Most natural humic solutions probably fall into the pH range of 4–9.

Phosphorus is held in solution as calcium phosphate by humus-bearing waters (Apushkin, 1935; Rankama and Sahama, 1949, p. 589), and is widely transported by such solutions. When phospho-organic solutions accumulate in stagnant environments such as bogs, hypolimnion parts of lakes, or in deeper oxygen-deficient parts of the ocean, phosphatic minerals may form when base flocculation of the organic matter occurs. Dietz, Emery, and Shepard (1942) described nodular phosphate deposition off the California coast, and Swain and Prokopovich (1954) and Swain (1956) described the occurrence of vivianite in lakes and bogs in Minnesota.

Humic solutions are of importance in the accumulation of *manganese* deposits. Manganese goes into solution in the bivalent state, and is held in humic waters, perhaps as the bicarbonate or as adsorbed $Mn(OH)_2$. Deposition of manganese may result, as in the case of iron, by flocculation of the associated organic matter or by loss of carbon dioxide. Because of the absorption of *potassium* by colloidal manganese hydroxide (Rankama and Sahama, 1949, p. 432), humus may play an indirect part in the enrichment of potassium in some sedimentary rocks. Although most of the alkali metal content (Li, Na, K, Rb, Cs) of living animals and plants probably is precipitated during decomposition, potassium is present in the more stable lipids and may persist in humus solutions.

Hydrogen sulfide gas associated with certain sapropels will precipitate *molybdenum* from molybdate solutions (Rankama, 1948, p. 402). The "shungite" from Shunga, Zaoneshye Peninsula, Karelo-Finnish S.S.R., is a Precambrian carbonaceous deposit which contains up to 50 g/ton MoO_3 and 100 g/ton WO_3 (Rankama and Sahama, 1949, p. 629). Other elements enriched in the shungite ash are Ti, V, Cu, Ni, Zr and Ba.

It is possible for *copper* minerals to be concentrated in humus sediments. The Permian Kupferschiefer of Germany probably represents deposition of copper sulfides in sapropelic muds from cupric sulfate solutions derived from the weathering of cupriferous rocks.

Silver has been found concentrated in bituminous *Dictyonema* shales of Scandinavia (Goldschmidt, 1931). Because silver is known to be concentrated by recent plankton, probably by adsorption, a similar cause may be suggested for Cambrian occurrences.

Certain coal beds and carbonized wood are host to concentrations of *germanium* (Goldschmidt, 1930). Peat bogs and coal beds have been investigated for deposits of germanium owing to interest in this metal for transistors (Breger, 1958).

Arsenic is probably concentrated to a certain extent in organic sediments but its biogeochemistry has not been investigated to any extent. Because arsenic tends to be enriched in coal ashes, the atmospheric humus around industrial areas is likely to contain concentrations of this element.

Sulfur is closely associated with humic materials in many instances, but despite its widespread occurrence it enters into organic reactions only to a limited extent. In other words, sulfur-bearing proteins and hydrocarbons utilize only a small part of the available sulfur in a sedimentary environment; most of it is present in the water as sulfate ion, which may be reduced to H_2S, precipitated with iron as ferrous sulfide hydrate, or oxidized to sulfur. The organic material and associated biochemical activity aid in the concentration of sulfur humus by maintaining low to negative redox potentials which retard the formation of insoluble sulfates. *Selenium* apparently can be concentrated as selenides together with sulfide, but selenium may occur separately from sulfur in carbonaceous rocks (Rankama and Sahama, 1949, p. 754).

Fluorine may be concentrated in organogenic phosphates, (Rankama and Sahama, 1949, p. 761) that have been deposited from humus colloids, and calcium fluoride is found in small amounts in bituminous limestones, as in the Ordovician of the Appalachian region. *Bromine* occurs in organic combination in soil and other humic materials. Kukersite, algal oil shale from Estonia, contains up to 132 g/ton of bromine. *Iodine* is concentrated in bituminous deposits, and enrichment of it in organo-phosphates and coal beds also occurs (Rankama and Sahama, 1949, p. 768).

Uranium concentrates in marine bituminous shales, carbonized plant remains, etc. (Breger and Deul, 1956).

Summary and Conclusions

In considering the definition and nature of humus it is necessary to take into account not only the obvious dark colored complex, but the colorless to light colored waxes, resins, hydrocarbons, nitrogenous compounds, etc., that typically are associated with the humus. Humus is formed more as a result of microbial activity than as a simple chemical transformation of plant and animal material.

Separation of fractions of humic substances is accomplished on an empirical basis into base-soluble humus, and insoluble humin; acidification of the humus solution produces a precipitate, humic acid, leaving fulvic acid in the solution; an alcohol-soluble fraction of the dried humic acid is called hymatomelanic acid.

Because of the uncertainty as to the origin of many specific examples of humus, there is no entirely satisfactory classification of humus at present. The fractionation described in the preceding paragraph is exceedingly unsatisfactory as a classification because from each of the fractions various substances such as sugars, phenols, etc., may be obtained depending on the source material and its state of decomposition. The genetic classification of Waksman at least has the advantage of arranging the humus into geological settings and is the one used in this discussion.

Humus and its fractions are not single substances and humus can be fractionated by dialysis and electrophoresis.

The antispetic property of humus is of geological importance in the preservation of various reactive organic substances associated with humus; merely anaerobic conditions are not responsible for the preservations in peat, lake, and marine humus. Phenols, quinones, phenol carboxylic acids, and phenol glucosides are among the compounds which act in a preservative and antiseptic capacity in peat.

The high water-holding capacity of humus materials is one of the most important of its physical properties; 85–95% or more of the weight of wet peat and copropel may be water. Shrinkage on drying is correspondingly great, but differs with the texture of the humus, coarse-fibered humus retaining more of its pore space and undergoing less shrinkage on drying than does copropel.

The colloidal nature of humus materials is important in the physical behaviour of humus solutions. Humus in part consists of particles about 0.02 μ in diameter which migrate in an electrical field with a negative charge. Brownian movement of particles can be observed in humus. Absorption of various metal bases and acids by humus colloids is characteristic; chemical reactions with the humus may occur following absorption of a certain amount of base. The movement of humic and associated inorganic substances (Ca, Mg, Fe, P, etc.) in sediments is probably affected by these properties. The acidity of the solution in which humus occurs governs the particle size of humus materials and their absorbed substances. Increase in acidity results in concentration of humus solutions, thus providing a mechanism for concentration of such mineral deposits as bog iron ore and phosphate. Humus also exerts a peptizing effect on clays and ferric hydroxides in suspension and retards the flocculating effects of electrolytes.

Ultraviolet absorption spectra of humus materials show that different molecules or micelle structures in different degrees of polymerization are involved in humus preparations (humic acid, hymatomelanic acid, etc.).

Humic acid preparations from sugars are not simple degradation products of sugar, i.e. furfural or hydroxymethylfurfural, as shown by their ultraviolet absorption spectra. The spectra of sulfuric acid hydrolyzates of humic acid, peat, copropel, and ancient bituminous sediments are identical, have maxima at 268 mμ, and indicate benzenoid structure.

The presence of phenolic hydroxyl groups in coal humic acid has been demonstrated by infrared absorption spectra (maximum at 3.25 μ) and chemical techniques.

X-ray investigations of various humus substances, including humic acid, have shown that only the aromatic graphite lattice is present, and in many instances of both natural and artificially prepared humus no development of graphitic structure has occurred. Aging of the humus generally increases the degree of graphite structure.

The distribution of carbon, nitrogen, carbohydrates, proteins, "lignins", and lipoids in various types of humus has been fairly well catalogued. All forms of humus show reduction in cellulosic substance and proteins and enrichment in "lignin" upon humification. Lipids decrease with humification, but hydrocarbons and resins (peat waxes) may increase. The best factor to use for converting the total organic carbon to total organic matter in humus is 1.724; but at best this is only an approximation. A specialized terminology has developed for kinds of humus that is partly genetic (lowmoor peat, forest peat), partly descriptive (gyttja, ävja), partly combinations of the two (copropel, humolimnic acid), and partly patrynomic or other polyglot (dopplerite, kukersite). Although a more concise classification would be desirable, the situation is not serious at present because of the limited number of investigators who utilize the more exotic terms.

Although the formation of humus is mainly microbiological, almost wholly chemical transformations of the following types may occur: (1) mineral acids may form hydroxymethylfurfural from carbohydrates and this in turn may condense to produce humus; (2) amino acids or polypeptides may condense with carbohydrates to form humus, for example melanoidin; (3) aldol condensation of methylglyoxal with amino acids may produce humic substances; (4) aromatic compounds such as phenol, quinone, and hydroxyquinone of natural occurrence may become oxidized to form humus. Other processes for the formation of humus mainly involve biochemical transformation of lignin into humus. Opening of heterocyclic lignin rings may lead to the formation of humic compounds.

Microbiological formation of humus evidently proceeds as follows: carbohydrates serve as the source of energy for the micro-organisms, the proteinaceous and hemicellulose cell substance is synthesized as a result of their activity and lignin also undergoes modification; altogether, these products form humus. Autolysis of the micro-organisms themselves may produce considerable amounts of humus. Fungi are important in the production of forest humus and, therefore, probably play a major role in humus formation in the regions of brown-water lakes and rivers. Bacilli are thought to be the most abundant micro-organisms in peat bogs.

A large number of known substances have been isolated from humus. Among the quantitatively more important of these are hydrocarbons, phenols, glycerol, carbohydrates, amino acids and polypeptides, pigments, organic and fatty acids, alcohols, and aldehydes. A host of other compounds still remain to be characterized. Techniques in chromatography, absorption spectroscopy, and mass spectrometry appear to offer most promise for identification of the small quantities of materials yet to be isolated from humus.

The largest bulk of material available for study in humus consists of the fulvic acid– humic acid– hymatomelanic acid–humin series. This material evidently consists of micelles of polymeric nature the basic structure of which is a simple five- or six-membered ring or condensed rings bridged by —O—, —NH—, —CH_2—, or —S— linkages, and having attached hydroxyl groups that provide acidity, hydrophilic character, base exchange capacity, and tannin-like character (i.e. react with proteins, etc.). Some authorities believe humic acids are derived primarily from lignin by ring opening; others suggest that carbohydrates and other substances besides lignin also play a part in the formation of humic acid. Considering that humic acids are widely associated with non-ligniferous source material, for example much of the settled plankton in lakes and seas, the latter hypothesis is favored here. Fulvic acid and humin probably represent respectively less highly polymerized and more condensed forms of humic acid.

An outstanding feature of humic acids is their content of nitrogen. A variable proportion of the nitrogen (50–75%) is hydrolyzable and is in the form of of amino acids. At present it is not known whether the amino acids are simply adsorbed on the humic acids or are part of the humic acid micelles; both may be true. The remainder is in the form of ammonia plus additional nitrogen that may occur in the form of amine bridges between the unit structures of humic acid. This nitrogen is unaffected by treatment with acid or alkali.

From the geological standpoint, humus is important in two principal ways: (1) as the mother substance for coal and oil shale; (2) as a transporting agent and precipitant for a number of elements.

The role of humus in coal is described elsewhere in the book. Oil shales of both marine and lacustrine origin hold tremendous quantities of combustible materials that have great possibilities for future use as fuels. Conversion of the kerogen in oil shales is largely a technological problem; the geologist however can conduct useful studies of the stratigraphic distribution of the rich oil shales, determine their origin and mode of deposition, and investigate their paleontologic, petrographic, and structural relationships to the surrounding rocks. The calculations of reserves are dependent upon such studies.

Although suggestions have been made as to the importance of humus as the source of petroleum, few data have been accumulated to substantiate this idea. The source materials for petroleum undoubtedly accompanied the deposition of marine humus, leading to the widespread recognition of dark colored carbonaceous shales as petroleum source beds. On the other hand it is well known that some large oil accumulations are not directly related to these humic source beds, i.e. to reef accumulations, etc. The part humus may play as a source material for hydrocarbons has not been adequately investigated.

Iron is the most important among the elements that are transported and concentrated through the influence of humus, probably being in the form of so-called colloidal iron humates. It seems probable that most of the iron found in iron formations and bog ores moved to the area of deposition in this manner; its history after reaching the depositional basin is complicated by numerous factors discussion of which is beyond the scope of this chapter.

Humic substances are directly involved in the formation of underclays, bauxites and laterites because they assist in removal of silica, iron, and bases from the weathering aluminum-bearing rocks.

Concentrations of many other elements result from processes involving humus. These include phosphorus, manganese, molybdenum, copper, silver, germanium, arsenic, sulfur, selenium, fluorine, bromine, iodine, and uranium. The association of certain metals with fossil porphyrins is described in another part of the book. Although there are generalized data on the cycles involving humus, a great deal of elementary work in biogeochemistry of mineral deposits remains to be carried out.

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CHAPTER 5

GEOCHEMISTRY OF KEROGEN*

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Introduction

THE term "kerogen" is derived from the Greek, meaning oil- or wax-forming (Crum-Brown, 1912). It may be defined as the insoluble organic matter occurring in sedimentary rocks.‡

Kerogen is the most common form of organic carbon in the earth. If the total volume of the earth's sedimentary rocks is 10^8 miles^3 (Pettijohn, 1949), and if the average density of this rock is 2.3 g/cm^3, the weight of all sedimentary rocks is about 10^{18} tons. Since it is estimated that these rocks average 0.3% kerogen, the kerogen content of the earth is roughly 3×10^{15} tons. Van Krevelen estimates the earth's total coal reserves to be 5×10^{12} tons. Thus, there is almost 1000 times as much kerogen as coal in the crust of the earth.

It is important to distinguish between kerogen and the soluble constituents of sedimentary rocks; the latter consist of much smaller molecules and include paraffinic, cycloparaffinic, and aromatic hydrocarbons as well as non-hydrocarbons. Some confusion in the literature has resulted from a few authors' use of "kerogen" in referring to both soluble and insoluble organic matter.

Previous attempts to determine the nature of kerogen were motivated by (1) the need for a better understanding of the structure and composition of kerogen in oil shales and torbanites; (2) the desire to know more about the relationship between kerogen and uranium occurrence in black shales; and (3) the desire to gain an insight into the relationship between kerogen and petroleum. This chapter will organize the available data from these studies and summarize the over-all geologic and chemical significance of kerogen. Data-poor areas will be indicated, along with fields in which rewarding investigations might be carried out.

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‡ The name "kerogen" was originally given to the organic matter of oil shales, torbanites, "kerosene shales", etc., which breaks down on destructive distillation into oil-like products. However, oil shales themselves are loosely defined as rocks that yield commercial amounts of oil on retorting. Exactly what constitutes a "commercial amount" of oil depends on a number of factors, including the state of retorting technology, the availability and price of crude oil in a particular area, the oil-shale reserves, and the mineability of those reserves. Since the dividing line between oil shales and other rocks is rather arbitrary, there appears to be no logical reason for restricting the name "kerogen" to a certain rock type. More recently the word has been applied in general to the organic matter in sedimentary non-reservoir rocks (Forsman and Hunt, 1958; Kinney and Schwartz, 1957; Takahashi, 1935).

Although, as will be shown, some types of kerogen closely resemble coal, the geochemistry of coal will be touched upon only lightly when necessary for purposes of comparison; Chapter 6 will deal with this subject in detail. The voluminous literature on shale oil has been only lightly treated in this chapter since much of it deals with the engineering or technological aspects of shale oil production and contains no fundamental data. Information from such sources has been used only insofar as it throws light on the nature of kerogen.

The discussion of kerogen has been divided into three parts: (1) methods for isolating or separating kerogen from the rock matrix, (2) its elemental composition, and (3) determination of its chemical constitution. Finally, conjectures will be made as to the substance's possible precursors and the role of geologic factors in transforming them into kerogen.

Isolation Methods

The presence of relatively large amounts of non-organic matter in sedimentary rock requires some concentration of the organic matter or kerogen before it can be characterized. Although it is relatively easy to determine the organic carbon content of kerogen in its native state, it is virtually impossible to determine the organic hydrogen or oxygen content with any degree of accuracy. Clays and other aluminosilicates in rocks contain considerable amounts of water whose elements would be included in analyses for hydrogen and oxygen. Although degradation studies of kerogen could be carried out in the presence of large amounts of mineral matter, such an approach would not be practical because of the large-scale equipment that would be required. Also, oxidizable minerals such as pyrite would interfere in degradation studies involving oxidizing agents.

The ideal method for separating kerogen from the inorganic matter in a rock should fulfill several requirements. First, essentially no chemical alteration of the kerogen should take place in the process. Second, the method should yield sufficient pure material for elemental analysis and degradation studies. Finally, fractionation of the kerogen should be avoided; that is, the kerogen concentrate obtained should be representative of the starting material.

In general, two methods have been used for isolating kerogen from its rock matrix: physical and chemical. Physical methods may be subdivided into float-and-sink techniques and methods based on wettability differences of the organic and inorganic constituents. Chemical methods include digestions of the rock with hydrochloric and hydrofluoric acids and various modifications. Because the success of any study of kerogen is so dependent on the reduction of the ash content to a low value, these isolation methods are considered in some detail.

Physical Methods

Flotation ("Float-and-sink") techniques. In this method the finely ground kerogen-bearing rock is centrifuged in liquid media with specific gravities intermediate to those of the kerogen and the mineral matter. This technique has been employed by a few workers with varying degrees of success. Hubbard *et al.* (1952) centrifuged an acetic acid-treated oil shale in carbon tetrachloride–benzene mixtures. After several fractionations they recovered about 2% of the original kerogen with an ash content of 9%. Dancy and Giedroyc (1950) obtained a slight separation with one oil shale sample but reported complete failure with a second sample. Himus and Basak (1949) failed to effect any separation with three different oil shale samples. Both carbon tetrachloride-benzene mixtures and aqueous calcium chloride solutions were employed in these tests. Luts (1928) also used calcium chloride solutions on Estonian Kukersite and reported that the ash content was reduced to 3%. Aarna and Lippmaa (1957) recently obtained similar results with an Estonian oil shale. Flotation concentration methods involving halogenated phenols have been the subject of at least two patents (Lemme, 1953).

From the conflicting results obtained by various workers it is apparent that the variables in the method have not been fully worked out. Surface effects, such as wettability or the presence or absence of adsorbed air on the particle surfaces, could account for the varying results. Differences in the rock mineralogy, of course, could also be a factor. Air adsorption appears to be the most likely possibility, inasmuch as the true specific gravity of kerogen (see below) is considerably higher than the density of solvents in which the best separations have been obtained.

Flotation (and differential wettability) techniques have at least two advantages over chemical methods: (1) The organic carbon, and hydrogen, nitrogen, and sulfur contents of the kerogen can be determined at various stages of concentration. When individual plots of these elements vs. ash contents are extrapolated to zero per cent ash, rather reliable values for the composition of mineral-free kerogen are obtained. (2) It is unlikely that the kerogen would be chemically altered.

The disadvantages of this method are the rather high ash contents obtained, even after repeated treatments, and the rather poor recovery of kerogen. It would not appear feasible to employ this method on rocks containing relatively low concentrations of kerogen.

Differential wettability method. This method, first reported by Quass (1939), is an adaptation of the Trent amalgamation process for separating mineral matter from coals. In the procedure the finely ground rock is ball-milled in the presence of water and a hydrocarbon solvent such as kerosene or mineral oil. Under the proper conditions the kerogen forms a paste with the kerosene, the mineral matter being wetted by and passing into the water layer. Quass, who worked with Australian torbanites, reported a reduction in ash content to as low as 5%. Himus and Basak (1949) tried the method on four different oil shales, but removal of mineral matter was attained in only one case. In this instance a high residual ash content (34%) was obtained. Dancy and Giedroyc (1950) obtained partial separation of mineral matter from two out of three oil shales that they examined. The residual ash contents were 13 to 34%. Because these three groups of workers did not report the weights of their fractions, the efficiency of the process cannot be evaluated from their results. Recently Deul (1956) processed five samples of non-oil shales by a modification of Himus and Basak's (1949) procedure. In two of the samples, over two-thirds of the original kerogen was recovered with 26% ash or less. In the other three samples, however, poor recoveries (2–5%) of kerogen were obtained.

As in the float-and-sink method, the ultimate composition of the kerogen can be estimated by extrapolating carbon, hydrogen and oxygen to zero per cent ash. However, it is evident from the results obtained by various workers that this method would have limited applications for isolating kerogen from rocks with low kerogen contents.

Chemical Techniques

Acid digestion. Although there are several variations, most of the techniques that have been used involve digestions with hydrochloric acid, hydrofluoric acid, and combinations of these acids. In the preferred method, the finely ground and organic solvent-extracted rock is placed in a container of inert material, and methyl or *iso*propyl alcohol is added until a pasty consistency is obtained. Container materials that have been used include platinum, lead, copper, Monel metal, and polyethylene. The latter material is particularly good because it is cheap and because reaction mixtures can be centrifuged directly in the container without transfer, eliminating loss of material. To avoid possible decomposition of the organic matter, digestions are best carried out at temperatures not exceeding that of a water bath. Digestion of the sample with hydrochloric acid prior to use of hydrofluoric acid is particularly recommended for carbonates and calcareous shales. This procedure removes calcium ions which otherwise form insoluble calcium acid fluorides (Fieldner *et al.*, 1919; Forsman and Hunt, 1958). Following the hydrochloric acid digestion and several washings of the sample by the centrifuge method, 50% hydrofluoric acid is introduced into the sample in portions to dissolve aluminosilicates. Loss of sample by frothing can be prevented by directing a thin stream of water from a wash bottle into the sample to break up the foam. When the reaction is complete, hydrochloric acid is added to the reaction mixture to prevent the precipitation of insoluble aluminum fluorides (Fieldner *et al.*, 1919; Forsman and Hunt, 1958). Following removal of the supernatant solution by centrifugation and washing of the sample with water, this process is repeated until all the clays are decomposed. A further digestion with hydrofluoric acid is then carried out on the steam bath to remove any remaining quartz.

The organic residue can be analyzed for its ash content, and the nature of the mineral impurities can be determined by X-ray powder diffraction or by other techniques. Common contaminants are pyrite, zircon, and other hydrofluoric acid-resistant minerals, in addition to insoluble fluorides formed during the digestions (Forsman and Hunt, 1958). Most of the gelatinous, insoluble fluorides can be removed by alternate digestions with ammonium carbonate* and hydrochloric acid.

Dilute nitric acid (1:3) has been used by a number of workers for the removal of pyrite from the kerogen residue. However, because this reagent nitrates and oxidizes kerogens its use should be avoided (Dancy and Giedroyc, 1950; Down, 1939; Himus and Basak, 1949). Only one method has been found for dissolving pyrite under relatively mild conditions–the zinc–hydrochloric acid digestion method first used by Himus and Basak (1949). These authors added hydrochloric acid in portions to a mixture of powdered zinc and the kerogen residue. Forsman and Hunt (1958), however, found that the reverse method of addition is more effective. In the latter procedure zinc dust is added in portions to a stirred suspension of the kerogen residue in concentrated hydrochloric acid. Although either method is quite effective in dissolving pure pyrite, the presence of organic material appears to inhibit the reaction. Several treatments with the zinc–hydrochloric acid reagent are usually necessary.†

The zinc digestions can be conveniently carried out in the polyethylene container used in the hydrofluoric and hydrochloric acid digestions. The dissolution of pyrite is indicated by the formation of hydrogen sulfide and the appearance of ferrous ion in the supernatant solution.

Although several workers have claimed that the acid digestion method causes chemical change in the kerogen, there is actually very little evidence that this takes place. By the use of flotation techniques, Hubbard *et al.* (1952) reduced the ash content of an oil shale sample to 8.7%. Digestion of this sample with hydrochloric acid reduced the ash content further to only 5.4%; the color of the residue changed from light brown to dark chocolate. This color change was cited as possible evidence of alteration of the kerogen structure. Luts (1928) obtained a kerogen concentrate in a similar manner. His sample, however, did not show color change on acidification with hydrochloric acid. Because the oil shale sample used by Hubbard undoubtedly contained a high percentage of colorless carbonates, the effect they observed may have been the removal of white inorganic material upon acidification.

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* The use of sodium carbonate in this step, which has been recommended by several workers, is to be avoided since it results in the formation of insoluble sodium fluosilicates (Forsman and Hunt, 1958).

† Commercial zinc dust sometimes contains carbonaceous material as an impurity (Blumer, 1957). For this reason it is best to test the zinc dust with hydrochloric acid prior to using it on kerogen samples.

Several authors have cited the loss of nitrogen during the acid concentration of kerogen as evidence for chemical alteration of the molecule. Forsman and Hunt (1958), however, showed that the loss of nitrogen could equally well be accounted for as inorganic nitrogen removed from the sample during acid treatment. Their results showed that, based on the weight of the rock, the loss of nitrogen was rather uniform, whereas calculated on the kerogen or total nitrogen basis, the results showed wide variations. The loss of nitrogen also depended upon the type of rock being treated. Shales, in general, lost the largest amounts of nitrogen. Calcareous shales and clay limestones lost intermediate amounts, and relatively pure carbonates showed little loss of nitrogen. From data reported by Dancy and Giedroyc (1950), comparable nitrogen losses based on the weight of the rock may be calculated. The latter workers isolated material having an odor characteristic of nitrogen bases from the acid washes of one of the three kerogen samples that they examined. However, the quantities were too small for positive identification.

From the standpoint of ash removal, the acid extraction techniques are generally better than the physical methods of separation. In general, quite low ash contents are obtained (Carlson, 1937; Dancy and Giedroyc, 1950; Down, 1939; Franks and Goodier, 1939; Guthrie, 1938; Himus and Basak, 1949; Kinney and Schwartz, 1957; Lissner, 1910; McKee and Goodwin, 1923; Narbutt, 1922; Waters, 1948). For organic-rich oil shales, the residual ash of concentrates obtained by these methods is generally 1–4%; rocks with lesser amounts of organic matter are more difficult to de-ash because of their relatively high proportion of acid-resistant minerals (Forsman and Hunt, 1958).

At best, all the concentration methods that have been developed so far are time-consuming, messy, and expensive. To quote Himus (1950) "There is no universally satisfactory method for the determination of the composition of kerogens in a kerogen rock; every sample must be the subject of special investigation." Dancy and Giedroyc (1950) state the problem in other words: "No method generally applicable for the removal of mineral matter from oil shales can be described, and variations must be made to suit individual samples." There is a real need for better general methods of kerogen concentration.

It is possible that combinations of acid and physical methods may result in improved methods for concentrating kerogens, particularly in the rocks with lower amounts of organic matter. One possible method might consist of disaggregating the rock with ultrasonic energy or with hydrochloric (in the case of carbonates) or hydrofluoric acid followed by a preliminary separation in heavy liquids. It would appear from the literature that aqueous calcium chloride solutions are better than mixtures of organic solvents. Care should be taken to select a medium with a specific gravity midway between that of the kerogen (see below) and of the mineral matter in order to achieve the maximum separation. High speed centrifuges that have recently appeared on the market might show definite advantages in attaining large separation forces. Extraction of bituminous material from the rock prior to centrifugation would tend to minimize "sticking" of the kerogen to the inorganic particles. The relative wettabilities of the kerogen and of the rock material are certainly factors to be considered. This statement is particularly applicable to pyrite which is wetted by some organic solvents Forsman (1953). Following the float-and-sink separation, further reduction of ash could be accomplished by digestions with hydrofluoric and hydrochloric acids. Additional float-and-sink separations followed by more acid treatments might be necessary in some instances.

Properties of Kerogen

Physical characteristics—*Appearance.* Kerogens as isolated from rocks are generally obtained as very fine amorphous soft powders that vary from dark brown to jet black in color, many showing a marked resemblance to coal dust (Forsman and Hunt, 1958). Under the microscope the bulk of the organic matter consists of light yellow to dark brown particles, sometimes having the appearance of macerated cellular material. Generally however, the bulk of the organic matter is unidentifiable. Descriptions of individual samples are given in a later section (Table 8).

Refractive index. The only data reported in the literature are those of Forsman and co-workers (1958). Refractive indices of powdered kerogen samples were measured by the oil immersion method. Table 1 lists these measurements and includes the indices of a few coals and other substances.

TABLE 1

Refractive Indices of Kerogens, Coals, Asphaltites, and Mineral Waxes

Kerogen	Refractive index	Asphaltites, Coals, etc.	Refractive index
Green River (papery) sh.	1.50	Ozocerite (Green River)	1.53
Traverse ls.	1.57*	Wurtzilite (Green River)	1.57
Green River (mahogany) sh.	1.60	Gilsonite (Green River)	1.61
Woodford sh.	1.61	Albertite	1.66
Caney sh.	1.64	Lignite	1.63
Traverse ls.	1.73*	Subbituminous coal	1.70
Frontier sh.	1.73	Bituminous coal	1.75
		Anthracite	1.80

* Separate fractions obtained during hydrochloric acid treatment in which part of the kerogen floated on the surface of the acid mixture.

Specific gravity. Specific gravities of only a few kerogen samples have been reported (Forsman and Hunt, 1958). Table 2 lists these values, which were obtained by the pycnometer method with isopropyl alcohol at 25°C.

Corresponding data for coals and other substances are included for comparison.

The specific gravity data listed in Table 2 have been corrected for mineral content, which consists chiefly of pyrite and insoluble fluorides. The pyrite content of the samples was estimated from the emission spectrographic determination for iron and from the sulfur content as determined by the Parr bomb method. The major fluoride contaminants were identified from their X-ray diffraction spectra, and semi-quantitative estimates of the percentages of these compounds were made from the emission spectrographic analyses for calcium, aluminum, and sodium. Published data on the specific gravities of pyrite and insoluble fluorides were used in calculating the corrected specific gravities of the kerogens.

TABLE 2

Corrected Specific Gravities of Kerogens, Coals, Asphaltites and Mineral Waxes*

Kerogen	Specific Gravity	Coals, Asphaltites, etc.	Specific Gravity
Frontier sh.	1.22	Ozocerite	0.85–1.0
Green River (mahogany) sh.	1.22	Gilsonite	1.03–1.10
Traverse ls.	1.32†	Albertite	1.07–1.10
Green River (papery) sh.	1.38	Wurtzilite	1.05–1.07
Cherokee sh.	1.39	Bituminous Coal	1.2–1.5
Traverse ls.	1.51†	Anthracite	1.4–1.8

* See text

† See footnote, Table 1.

Infrared spectra. Infrared spectra of kerogen samples have been published by only three groups of authors (Forsman and Hunt, 1958; Kasatochkin and Zil'berbrand, 1956; Kinney and Schwartz, 1957). A comparison of the spectra indicates that somewhat more definitive patterns are obtained when kerogens of low ash content are used. Forsman and Hunt (1958) observed that the C—H peaks at 3.5 and 6.9 μ of the Green River oil shale kerogens were slightly more intense than those of the other kerogen samples that were examined. This effect was attributed to a less highly condensed and more paraffinic structure in the Green River kerogen. The spectra of the Chattanooga black shale kerogen obtained by Kinney and Schwartz (1957) are interpreted by these authors to indicate the presence of hydroxyl groups (2.95 μ) and carbon–carbon double bonds (6.2 μ). However, the 6.2 μ peak could also be caused by conjugated carbonyl groups such as in quinones (Friedel and Queiser, 1956). The possibility of infrared absorption by aromatic nitro substituents was not considered by these authors. Unfortunately, nitrogen determinations were not made on the Chattanooga kerogen, so that it is not possible to ascertain whether nitration of the kerogen took place in the presence of a fairly concentrated nitric acid that was used in removing the pyrite.

Kasatochkin and Zil'berbrand (1956) examined the infrared spectra of two kerogen concentrates and observed that (1) very few methyl groups are present; (2) typical carbon–carbon double bond adsorption occurs at 6.25 μ; (3) condensed aromatic rings are absent (no 12–13.5 μ bands); (4) methylene groups are present; (5) some carboxyl groups exist and are confirmed by the reaction with barium hydroxide; and (6) the intense 8μ micron band indicates considerable carbon-to-oxygen bonds. One kerogen sample also had bands at 6.65 (aromatic rings) and 3.25 μ (aromatic carbon–hydrogen). According to the interpretation, the kerogens contain condensed substituted aromatic rings with methylene side chains, and have considerable oxygen contents.

Elemental composition—Kerogen in rocks is made up of the elements carbon, hydrogen, nitrogen, oxygen, sulfur, and possibly phosphorus and metals. The major elements, however, are carbon, hydrogen, and oxygen. Nitrogen is a relatively minor constituent of kerogen on either an atomic or weight basis.

As a result of the isolation and elemental analysis of kerogen by a number of workers, sufficient data have been accumulated to give some insight into the nature of kerogen. Approximately fifty analyses of kerogen have been reported representing samples from about thirty-three areas; about one-half of the samples are oil shales. A major part of the work on isolation and analysis of kerogen in oil shales and torbanites has been carried out by G. L. Himus and several of his students in London. Most of the work on non-oil shales has been done by Forsman and co-workers (1958).

Carbon, hydrogen and oxygen content. Because these three elements make up most of the kerogen molecule, it is to be expected that variations in the distribution of these elements would tend to show the greatest differences between kerogens of various types. Although the analysis of relatively mineral-free kerogen for carbon and hydrogen is straightforward it is only recently that the direct methods for analyzing organic oxygen have been available. Consequently, in most of the literature on kerogens and coal composition the oxygen contents reported have been determined by difference (one hundred minus the sum of the elements and the ash). Thus, "oxygen" obtained by difference is really the oxygen content plus errors in all the analyses, including that in the mineral content. A particularly troublesome source of error lies in the mineral content, which is difficult to determine directly. Several formulae have been proposed and some adopted for converting ash value to mineral content of coals, however, these formulae cannot be applied to kerogens because of the widely varying organic composition of kerogen residues. Relatively inexpensive and reliable methods, such as the Unterzaucher analysis, have been developed for direct oxygen determinations. Consequently, there is little reason now to determine oxygen in kerogen (or coals) by difference. The Unterzaucher method is particularly adaptable because metallic oxides give little interference.

In Table 3 are shown the elemental compositions of kerogens taken from the literature. With the exception of data reported by Forsman and coworkers (1958), oxygen values have been determined by difference. The carbon, hydrogen, and oxygen values as reported by the various authors have been normalized so that their sum totals 100%. Wherever analyses of more than one sample from the same general area are reported, these data are gathered into a single value to eliminate, insofar as possible, errors due to the uncertainty of the oxygen value. In obtaining composite values from more than one sample (such as in the case of the Kimmeridge, Lothian, Amherst, Ermelo, Kukersite, Green River, and Australian torbanite samples) the individual points were plotted on triangular diagrams, lines were drawn connecting the points so as to make triangles, and the best values were selected by picking a point near the center of the triangles.

Some samples, such as the Ermelo torbanites, vary considerably in composition. Himus (1950) attributes this to the varying proportions of two different types of kerogens in the samples. Because of this variation, compositions listed in Table 3 are to be regarded as representative or average values for the kerogen in a given area.

The ultimate composition of kerogen shows no relationship to geologic age, as can be seen from Table 3 in which the samples are arranged by increasing geologic age. The two Tertiary shales from Brazil, for example, encompass almost the entire spread of values in the table. The geologic and environmental significance of compositional data will be discussed in a later section.

Nitrogen. Table 3, which also lists the atomic carbon–nitrogen ratios of the kerogen samples, indicates that with a few exceptions these ratios are remarkably constant. Most of the carbon–nitrogen ratios vary by a factor of only 2 or 3. Because there is only one atom of nitrogen for fifty carbon atoms in the kerogen molecule, nitrogen is relatively unimportant in the chemistry of the kerogen as a whole. The carbon–nitrogen ratio appears to be unrelated to lithology, geologic age, or any of the other common geologic parameters.

There are a few exceptions to the consistency of the carbon–nitrogen ratio in Table 3. The Australian samples and the Estonian Kukersite appear to be low in nitrogen compared with most of the other samples. The Wilcox and Frontier shales have very high and nearly identical carbon–nitrogen ratios. The carbon, hydrogen, and oxygen contents of these two samples also are very similar. The kerogen from the Morrison shale also appears to have a low carbon–nitrogen ratio, possibly due to inorganic nitrogen, such as ammonium ion, in the high ash content of the sample.

Occasionally it has been possible to separate more than one type of kerogen from the same sample. Such was the case of the Eocene Wilcox

TABLE 3
Elemental Composition of Kerogens

Name and Location	Geologic Age	Composition			Atomic	References (see foot of table)
		C, %	H, %	O, %	C/N	
Amherst, Burma	M. Tertiary	79.0	11.2	9.8	70–72	(1, 2, 3, 4)
Monterey sh., Calif.	Miocene	83.0	8.4	8.6	35	(5)
Oil shale, Australia	Tertiary	83.1	10.4	6.5	120	(6)
Cypris sh., Brazil	Tertiary	80.2	11.8	8.0	70	(7)
Massive sh., Brazil	Tertiary	68.5	8.5	23.0	59	(7)
Kohat, India	L. Tertiary	74.2	8.3	17.5	63	(1, 2)
Green River, Colo. and Utah	Eocene	82.2	10.1	7.8	34–6; 61	(5, 6, 8, 9)
Green River, Nevada	Eocene	87.5	8.7	3.8	59	(6)
Um-Barek, Israel	Cretaceous	77.8	7.9	14.3	25	(10)
Wilcox sh., La.	Eocene	80.3	5.4	14.3	520	(5)
Frontier sh., Wyo.	Cretaceous	81.8	6.1	12.1	575	(5)
La Luna ls., Colombia	Cretaceous	89.6	7.2	3.2	52	(5)
Kimmeridge, England	Jurassic	77.0	8.0	15.0	52–71	(2, 3, 11, 12, 13)
Morrison sh., Wyo.	Jurassic	75.1	7.3	17.6	20	(5)
Wurtemberg sh., France	Jurassic	83.1	9.0	7.9	64	(14)
Torbanite, Australia	Permian	86.2	10.6	3.2	100–320	(3, 15, 16, 17, 18, 19)
Kounova sh., Czechoslovakia	Permian	82.5	9.5	8.0	65	(20)
Ermelo sh., S. Africa	Permo-Carbonif.	82.0	8.2	9.8	44–93	(11, 12, 21, 22, 23)
Tasmanite, Tasmania	Permo-Carbonif.	82.7	10.7	6.6	152	(19, 24)
St. Hillaire, France	Permo-Carbonif.	87.2	7.9	4.9	71	(11)
Autun, France	Permo-Carbonif.	84.3	8.4	7.3	36	(7)
Plzen, Czechoslovakia	Permo-Carbonif.	86.1	7.8	6.1	69	(20)
Lothian oil sh., Scotland	Carbonif.	82.0	8.5	9.5	29–41	(3, 12)
Cherokee sh., Kan.	Pennsylvanian	88.2	5.1	6.7	42	(5)

TABLE 3—*continued*

Name and Location	Geologic Age	Composition			Atomic	References (see foot of table)
		C, %	H, %	O, %	C/N	
Madison dolo., Wyo.	Mississippian	88.1	5.0	6.9	48	(5)
Ste. Genevieve ls., Ky.	Mississippian	81.9	6.5	11.6	33	(5)
Caney sh., Okla.	Mississippian	80.1	7.0	12.9	30	(5)
Woodford sh., Okla.	Mississippian	88.3	6.7	5.0	31	(5)
Chattanooga sh., Kentucky	Devonian	82.6	8.7	8.7	42	(6)
Traverse ls., Mich.	Devonian	86.2	8.2	5.6	44–61	(5)
Duvernay sh., Alta.	Devonian	86.7	9.0	4.3	52–70	(5)
Kukersite, Estonia	Ordovician	79.3	10.0	10.7	180–920	(2, 3, 25, 26, 27, 28)
Collier ls., Ark.*	Cambrian	95.8	2.7	1.5	113	(5)
Phyllite, Texas*	Paleozoic	93.2	3.0	3.8	570	(5)

* Metamorphosed rock

(1) Down, 1939.
(2) Down and Himus, 1941.
(3) Himus, 1941.
(4) Himus and Basak, 1949.
(5) Forsman and Hunt, 1958.
(6) Guthrie, 1938.
(7) Kapur, 1950
(8) Hubbard *et al.* 1952.
(9) Schnackenberg and Prien, 1953.
(10) Gil-Av *et al.*, 1954
(11) Dancy and Giedroyc, 1950a
(12) Down, 1939a.
(13) MacDougall and Cawley, 1923
(14) Couderc, 1950.
(15) Cane, 1943.
(16) Cane, 1946.
(17) Dulhunty, 1943
(18) Rogers and Cane, 1945.
(19) Waters, 1948.
(20) Himus and Basak, 1949.
(21) Blelock, 1931.
(22) Petrick, 1936.
(23) Quass, 1939
(24) Jeffrey, 1915.
(25) Fisher *et al.*, 1940
(26) Kogerman and Kopwillem, 1932.
(27) Luts, 1934.
(28) Luts, 1938.

sample (Table 4) in which the concentrated kerogen was separated into a fine and a coarse fraction by sieving (Forsman and Hunt, 1958). Although the carbon, hydrogen, and oxygen contents of these two fractions are very similar, the atomic carbon–nitrogen ratios indicate that these two fractions may be basically different. Since both fractions have been subjected to the same degree of metamorphism or maturation, a similarity in carbon, hydrogen, and oxygen compositions would be expected.

In the St. Genevieve Limestone, one kerogen concentrate was obtained from the matrix of the rock, while a second fraction was isolated from a stylolite a few inches away (Table 5). In this case, a close similarity was found in both the carbon–hydrogen–oxygen composition and the carbon-to-nitrogen ratio (Forsman and Hunt, 1958). The over-all similarity of these two fractions lends support to the post-induration solution theory of stylolite formation (Dunnington, 1954).

TABLE 4

Normalized Elemental Composition of Kerogen Fractions in Wilcox Shale

Fraction	C, %	H, %	O, %	Atomic C/N
Fine	80.3	5.4	14.3	520
Coarse	78.4	6.3	15.3	29

TABLE 5

Normalized Elemental Composition of Kerogen in Ste. Genevieve Limestone Matrix and Stylolite

Fraction	C, %	H, %	O, %	Atomic C/N
Matrix	81.9	6.5	11.6	33
Stylolite	80.5	7.2	12.3	24

Sulfur and metals. Although kerogen undoubtedly contains sulfur in organic combination, it is difficult to obtain quantitative results because most methods determine both inorganic and organic sulfur. Because of the difficulties in separating pyrite completely from kerogen, up to one half of the total sulfur reported by various authors in kerogen samples may be pyritic (cf. Gil-Av *et al.*, 1954). A satisfactory method for quantitative removal of pyrite without altering the kerogen molecule would greatly aid our understanding of the sulfur chemistry of kerogen.

It is entirely possible that some metallic elements may be organically combined in the kerogen structure, although there is no data to support this suggestion. Forsman (1953) detected a number of different metals in kerogen residues. Most of these metals, however, were probably associated with the heavy minerals that resisted acid treatment. Down (1939a) found that a certain amount of iron in one of his kerogen residues resisted attack by the reagents used in removing the pyrite, and for this reason felt that iron was organically combined. It is possible, of course, that the iron in this sample could have been in pyrite that resisted attack because of the protecting action of the organic matter. In situations such as this an X-ray powder diffraction spectrum of the sample is very useful in determining if pyrite is present.

Determination of organic content of rocks. In many instances studies of the relationship of the organic content of rock to other parameters can be made satisfactorily on the basis of the organic carbon content. For some purposes, however, such as in making material balances, it is desirable to know the total organic content of a rock. This value can be obtained readily in petroleum reservoir rocks whose organic matter is largely soluble in organic solvents. For typical kerogen rocks, however, no direct method is available.

In the past the total organic content of a rock has been calculated by multiplying the per cent of organic carbon by a suitable number, termed the organic factor. An accurate value for the organic factor is difficult to obtain from elemental analyses of a rock itself, chiefly because of the water content of the rock, which affects both the hydrogen and oxygen analyses.

For a number of years investigators have used the value 1.6 as the organic factor for ancient rocks. This value was originally proposed by Trask and Patnode (1942) on the assumption of a mean value of 23% oxygen in sedimentary organic matter. More recent work has shown that this value is about 30% high (Forsman and Hunt, 1958).

The revised organic factor (1.22) is an average of data on twenty individual samples obtained by summing the organic constituents of the kerogen and dividing by the total organic carbon. This value agrees within 2% of the organic factor calculated from data given by Himus (1950). For kerogen in metamorphosed rocks, Forsman and Hunt (1958) suggest the use of a somewhat lower value (1.07).

Constitution of kerogen—In the foregoing discussion it has been shown that, on the basis of elemental composition, broad differences exist between kerogens. However, carbon, hydrogen, and oxygen compositions give only a very crude picture of the kerogen structure. It is entirely possible that two kerogen samples with comparable elemental compositions could have basically different structures. Without some idea as to the constitution of kerogen, it would be virtually impossible to state the types of organic substances that may have been the precursors of kerogen.

In ordinary organic constitutional analysis the structure of an organic compound is generally determined by step-wise degradation of the substance to the point at which identifiable compounds are obtained. By mentally reconstructing these fragments, a guess is made as to the original structure; attempts are then made to confirm the structure by synthesis. However, as pointed out by van Krevelen and Schuyer (1957) the confirmation of structure by synthesis is impossible in the case of coals because there would be few criteria for comparing the natural with the synthetic product. It might be added that the same statement also holds for kerogen.

Despite these almost insurmountable difficulties, attempts have been made to degrade the kerogen molecules, and much useful information has been gained. The methods that have been used were (1) oxidation, (2) hydrogenolysis, (3) pyrolysis, and (4) functional group analysis. Physical constitutional methods that have been extensively applied in the constitutional analysis of coals (van Krevelen and Schuyer, 1957) have not been used for kerogens but appear to offer considerable promise.

Oxidative degradation. The use of oxidizing agents in the controlled oxidation of kerogen has been limited to oxygen (or air), hydrogen peroxide, ozone, and potassium permanganate. Several other oxidizing agents, including nitric acid, and anodic oxidations, have been used on coals with varying degrees of success, but have not yet been applied to kerogens.

Alkaline permanganate oxidation, one of the classical methods of studying constitution, has been used for many years. Bone and Himus (1936) developed the "carbon balance" and "bulk oxidation" methods for determining the constitution of coal. They showed that in the oxidation of lignin and members of the peat-to-anthracite series increasing amounts of benzenoid acids were formed. In particular, the yield of mellitic (benzenehexacarboxylic) acid has been shown to increase with increasing rank of coals (Juettner, 1937).* These results are important because they confirm other evidence that the maturation of coal involves cyclization to form progressively more highly condensed aromatic ring systems.

Using similar techniques, several workers have studied the constitution of a few oil shale kerogens. Table 6 summarizes the results of these studies and includes, for comparison, data obtained by Bone and Himus (1936) on the oxidation of lignins and members of the peat-to-anthracite series.

The kerogen oxidation results are somewhat difficult to compare with those of the coals because the kerogen could not be oxidized completely within a reasonable time. Possibly the oxidation rate could be increased by using more nearly ash-free kerogen samples. Modified methods for removing soluble products from the zone of oxidation as soon as they were formed might also be helpful.

Table 6 summarizes the results of kerogen oxidations and classifies the samples according to the presence or absence of benzenoid acids in the products. Calculated on the basis of the amount of carbon oxidized, the distributions of oxidation products are surprisingly uniform, although they

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* This particular series of experiments, however, was carried out with nitric acid as the oxidizing agent.

TABLE 6

Permanganate Oxidation of Coals and Kerogen

Substance	Time, hr	Elemental carbon distribution, % of carbon oxidized				Un-solubilized carbon, % of kerogen carbon	References
		CO_2	Volatile acids*	Oxalic acid	Non-volatile. (non-oxalic) acids†		
Lignins, peats and coals							
Lignins	50–60	59	5	22	14	—	Modified from (1)
Peats		55	4	23	18	—	
Brown coals, lignites		51	5	15	29	—	
Bituminous coals		40	3	14	43	—	
Anthracite		43	2	7	48	8	
Kerogens yielding benzenoid acids							
Kimmeridge	30–56	50	8	30	12	1	(2,3)
Kohat	132	47	4	33	16‡	7	(2)
Lothian (average of 3 spls.)	125	47	7	22	24	46	(2)
St. Hillaire	100	60	1	14	25	45	(3)
Ermelo	125	46	8	20	26	34	(2,3)
Kerogens yielding no benzenoid acids							
Kukersite	145	55	9	32	4	9	(2)
Gdov	500	94	2	3	1	0	(4)
Amherst	115	55	4	36	5‡	25	(5)
Green River	100	55	2	42	1	4	(6)
Volga	500	87	4	5	4**	0	(4)

* Mostly acetic acid

† Includes benzenoid acids plus, in some cases, more complex, heterocyclic acids

‡ Benzenoid acids not looked for

** Benzenoid acids indentified in oxidation products. However, because of the very low benzenoid acid content, this kerogen must be regarded as essentially non-benzenoid.

[1] Bone and Himus, 1936.

[2] Down and Himus, 1941.

[3] Dancy and Giedroyc, 1950b.

[4] Lanin and Pronina, 1944.

[5] Dineen, 1954

[6] Robinson *et al.*, 1953.

do not show this uniformity when calculated on the basis of the original kerogen. In the kerogens that yield benzenoid acids on oxidation, the carbon dioxide carbon, with one exception, varied between 46 and 50%.

In the kerogens that yield essentially no benzenoid acids, the CO_2 carbon was about 55%. Unfortunately, the Gdov and Volga samples were subjected to much longer oxidation periods than the other samples, so that these results are not directly comparable. The amount of carbon appearing in the non-volatile, non-oxalic acid fractions in the benzenoid-acid kerogens was relatively high (12–26% of the carbon oxidized). In contrast, the non-benzenoid acid types yielded practically none of this type of acid.

Comparison of the kerogen oxidation data with those of lignins, peats, and coals leads one to suspect that the benzenoid–acid kerogens are coal-like in nature. It is true that the amounts of oxalic acid formed from these kerogens are somewhat higher than those formed from the coal series. This, however, may be a consequence of the longer reaction times necessary for the kerogens, and it may be that the oxalic acid was formed at the expense of the non-volatile, non-oxalic acids. The non-benzenoid acid kerogens are quite different from coals, chiefly in the amount of non-volatile, non-oxalic acid fraction formed.

The rather large fraction of kerogen that apparently resists oxidation in the Lothian, St. Hillaire, Ermelo, and Amherst samples has led some authors to postulate the existence of two types of kerogens in these rocks (Dancy and Giedroyc, 1950b; Down and Himus, 1941). The oxidation residue from the Ermelo sample was shown (Dancy and Giedroyc, 1950b to be very similar in elemental composition to that of typical Australian torbanites. The kerogen in the latter is thought to be almost purely algal in origin (Cane, 1946). Moreover, the Ermelo oxidation residue showed a very pronounced similarity under the microscope to the yellow bodies ("fossil algae") in the Australian torbanite. The black kerogen fraction in the original Ermelo sample had completely disappeared during oxidation. Unfortunately, the behavior of Australian torbanites toward permanganate was not studied by these authors, and no data on comparable material have been published. These authors also made the rather interesting observation that the proportion of kerogen in the Ermelo oxidation residue convertible to oil was almost double that of the original kerogen. The increase in oil yield was attributed to the concentration of fossil algae in the sample by oxidation.

Kogerman (1952), who studied the rate of permanganate oxidation of Estonian Kukersite at various temperatures and hydroxide concentrations, concluded that the reaction is second order. In confirmation of the results of Down and Himus (1941) as well as those of earlier studies (Kogerman (1938), no benzene-carboxylic acids were identified in the reaction products. Ketonic and lactonic acids, however, were reported.

Fomina and Pobul (1955) studied mild permanganate oxidation products of Kukersite by silica gel chromatography. These authors also found little evidence of benzenoid structure. Dibasic acids higher than oxalic (succinic, glutaric, adipic, pimelic, suberic, and azelaic) accounted for more than 20% of the solubilized kerogen.

Working with Green River Shales, Robinson *et al.* (1956), obtained results strikingly similar to those of Fomina and Pobul (1958). The crude acids were converted into their butyl esters, which were fractionated by vacuum distillation. The dibasic acids were identified by mass and X-ray diffraction methods and included oxalic, succinic, glutaric, adipic, pimelic, suberic, and traces of azelaic. About 17% of the carbon in the solubilized kerogen was represented by acids higher than oxalic. There was no evidence for the presence of even traces of aromatic acids, although considerable amounts of substances that appeared to be ketonic or *cyclo*-paraffinic dibasic acids were obtained.

Only a limited amount of work has been done with oxidizing agents other than permanganate. Dancy and Giedroyc (1950b) made some preliminary experiments with gaseous oxygen at 150°–200°C. As in the case with coals, acids were produced which were partially characterized by elemental analysis and infrared spectra. The action of permanganate on the Ermelo kerogen was quite different from that of oxygen, which tended to destroy the oil-yielding or algal portion of the kerogen. Kinney and Schwartz (1957) studied the oxidation of Chattanooga black shale with air at 200°C. From infrared evidence the authors concluded that the acids formed from this sample were quinoid in nature; however, the authors were unable to rule out the possibility that the infrared absorption bands might equally well be related to aromatic structures. Kinney and his students later used ozone in similar studies.

Dancy and Giedroyc (1950b) also studied the effect of hydrogen peroxide as an oxidizing agent on one sample of kerogen. Again a range of complex acids was obtained. A small amount of low molecular weight acids was identified; in general, these acids were the same as those found by permanganate oxidation. Infrared absorption spectra of the"intermediate acids" from the Kimmeridge kerogen showed the presence of aliphatic unsaturation, particularly conjugated dienes. The existence of a substantial amount of organic sulfur as an integral part of the kerogen molecule was also indicated.

Oxidation studies indicate that there may be as many as three types of kerogen in rocks. The first of these types bears a strong resemblance to humic matter found in lignins, peats, and coals. A second type, which occurs in Australian torbanites, appears to be of algal origin. In some rocks, this type of kerogen appears to be mixed with varying amounts of coaly-type kerogen and apparently is the major source of shale oil. A possible third type of kerogen of questionable origin is exemplified by Green River and Kukersite deposits. This type, however, also yields oil on pyrolysis.

Further work on oxidative degration could yield some very useful results. Particular attention should be paid to reagents less severe than alkaline permanganate, which converts a large fraction of the organic matter to carbon dioxide. Much more work is needed on the determination of structure of the "humic" acids, the initial breakdown products of kerogen. These substances are largely undistillable even in the form of their methyl esters. Elution or partition chromatography might be a convenient method of separating these rather intractable materials, although these methods are largely untried. All the oxidation experiments have been restricted so far to the coals and very rich oil shales. Oxidation studies of the kerogen in more typical rocks is sorely needed. A major problem will be the preparation of sufficient amounts of concentrate to carry out these studies.

Hydrogenolysis. This method has been used extensively with coals on a commercial scale, although only to a limited extent for purposes of characterization or determination of structure. Very few studies have been made with kerogen.

Kogerman and Kopwillem (1932), who hydrogenated a sample of Estonian Kukersite at 375°–450°C and 190–290 atm, found that the amount of kerogen liquified was approximately equivalent to the amount of oil obtained on pyrolysis. About 50% of the kerogen was solubilized; the soluble products consisted of 12% gasolines, 17% kerosenes, and 20% asphalt. The kerosene fraction included 13% higher phenols, 32% unsaturated hydrocarbons, and 8.5% aromatics. Prien (1948) reports some preliminary data on the hydrogenolysis of Green River oil shale at 100–270 atm and 270°–450°C. Qualitative observations are made regarding the conditions for optimum yield of soluble products, although no quantitative data are given. Hydrogenolysis of a kerogen concentrate from a Baltic shale is reported to yield distillable products (Lozovoi, 1957).

Forsman and co-workers hydrogenated several representative kerogen samples and a bituminous coal at 360°–400°C and 180–220 atm in the absence of a catalyst (Forsman and Hunt, 1958). Normal heptane was used as a carrier in these experiments. These temperatures are sufficiently high that cleavage of carbon–carbon and carbon–oxygen bonds can take place, but are low enough to prevent polymerization of the solvent or of the coal degradation products. The results of these experiments (Fig. 1) show that there are very marked differences to be found between kerogens. The non-coaly La Luna and Green River kerogens are clearly different from the coaly-type Wilcox kerogen in the amount of kerogen converted to soluble products. The hydrogenolysis products of the La Luna and Green River samples are quite dissimilar in the distribution of their hydrocarbon and asphaltic contents.

In view of the wide variations in the distribution of products obtained with different kerogen samples, the marked similarity between the hydrogenolysis products of the Wilcox kerogen and the bituminous coal appears especially significant. The Wilcox shale was deposited in a near-shore environment in an area of numerous transgressions and regressions of the sea (Culbertson, 1940), where coal formation would be expected to take place during certain portions of these cycles. The section from which the Wilcox samples was taken consists of fairly thin alternating beds of shales, lignitic shales, and coals (Forsman, 1953).

Unlike the other kerogen samples, the soluble products from the kerogen of the metamorphosed Collier Limestone consisted predominantly of hydrocarbons, and over four-fifths of this kerogen resisted attack by hydrogen. These findings agree with the observation that the coal molecule becomes more inert with increase in rank. In particular it has been observed that the hydrogenolysis products from samples of higher rank tend to have lower oxygen contents and lower hydrogen to carbon ratios. Also, the yield of soluble products is known to decrease with increasing rank (Weiler, 1945). Although the reaction products obtained from the kerogens were only partially characterized, an indication of their compositions may be gained from the ratio of paraffin and naphthenes to aromatics (Table 7). In comparison with the other samples, the bituminous coal and Wilcox kerogen products have very low ratios. The result for the coal sample is in essential agreement with findings of other workers, who report that the predominant products in the hydrogenolysis of coal are aromatics (Weiler, 1945).

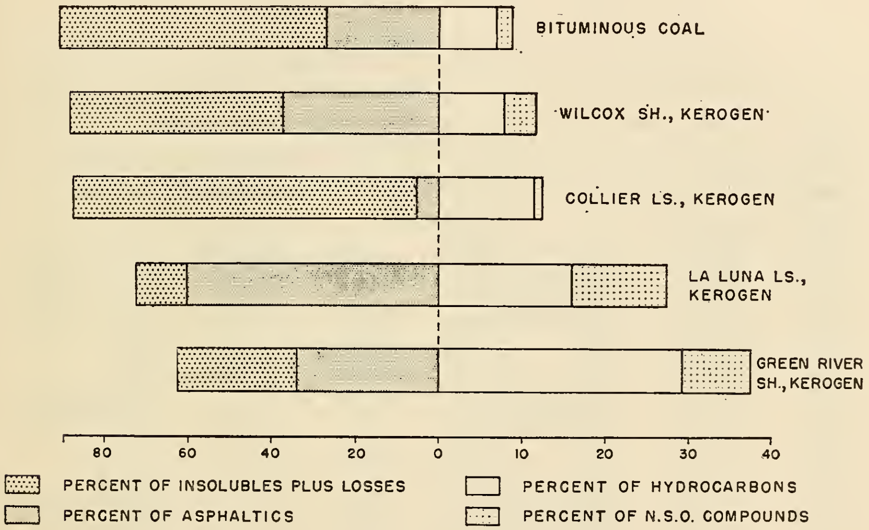


FIG. 1. Distribution of hydrogenolysis products of kerogen and coal.

The chief value of hydrogenolysis appears to be in showing empirical similarities or differences between kerogens. There is some doubt, however, as to its utility in actual structure determinations because of the possibilities of molecular rearrangements and transformations under the drastic conditions employed. Hydrogenolysis has proved to be of only limited usefulness in the elucidation of coal structure although it does afford additional evidence for the polynuclear structure of coal.

Thermal decomposition. Quite a number of methods have been developed for pyrolyzing the kerogen in shales both on a laboratory and a commercial scale to obtain the distillates known as shale oils. Like petroleum, the products include hydrocarbons plus nitrogen, sulfur, and oxygen derivatives of the hydrocarbons. However, shale oil differs from petroleum in that non-hydrocarbons are present to a much greater extent, particularly in the higher boiling fractions. In addition, the hydrocarbons in shale oil are much more unsaturated than those in petroleum.

TABLE 7
Distribution of Hydrocarbon Types Formed in Kerogen and Coal Hydrogenolysis

Sample	Paraffin–naphthenes/Aromatics
Wilcox kerogen	0.10
Bituminous coal	0.13
La Luna kerogen	0.65
Green River kerogen	1.20
Collier kerogen	1.60

The amount of the total kerogen converted to liquid and soluble products, the distribution of the molecular types and weights in the products, and the sulfur and nitrogen content show considerable variations depending upon the conditions of pyrolysis. In particular, variables that are known to affect these properties include the specific retorting method used, the temperature, the particle size of the shale, the rate of heating, and the

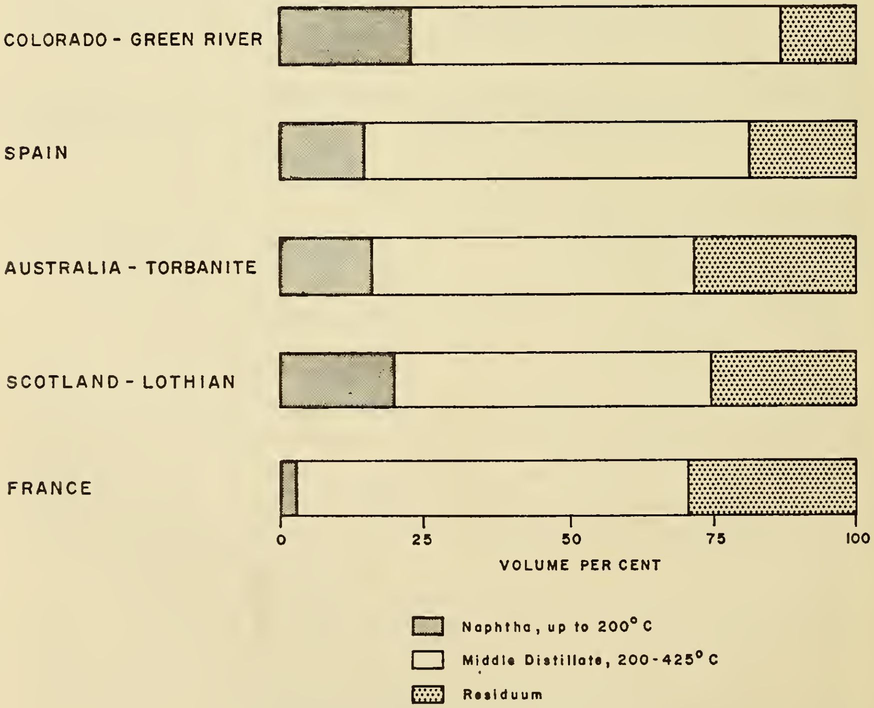


FIG. 2. Distillation analysis of shale oils.

mineralogy of the shale. (The latter variable has been disputed by some authors.) Some of the major variations in composition may be correlated with the source of the shale and the temperature used during pyrolysis (Dineen *et al.*, 1952). The sulfur and nitrogen contents seem to depend primarily on the source of the shale. At relatively low pyrolysis temperatures the hydrocarbon distributions seem to depend mainly on the source of the sample, but with increasing temperatures the aromaticity of the oil increases to the point at which non-aromatics are virtually absent.

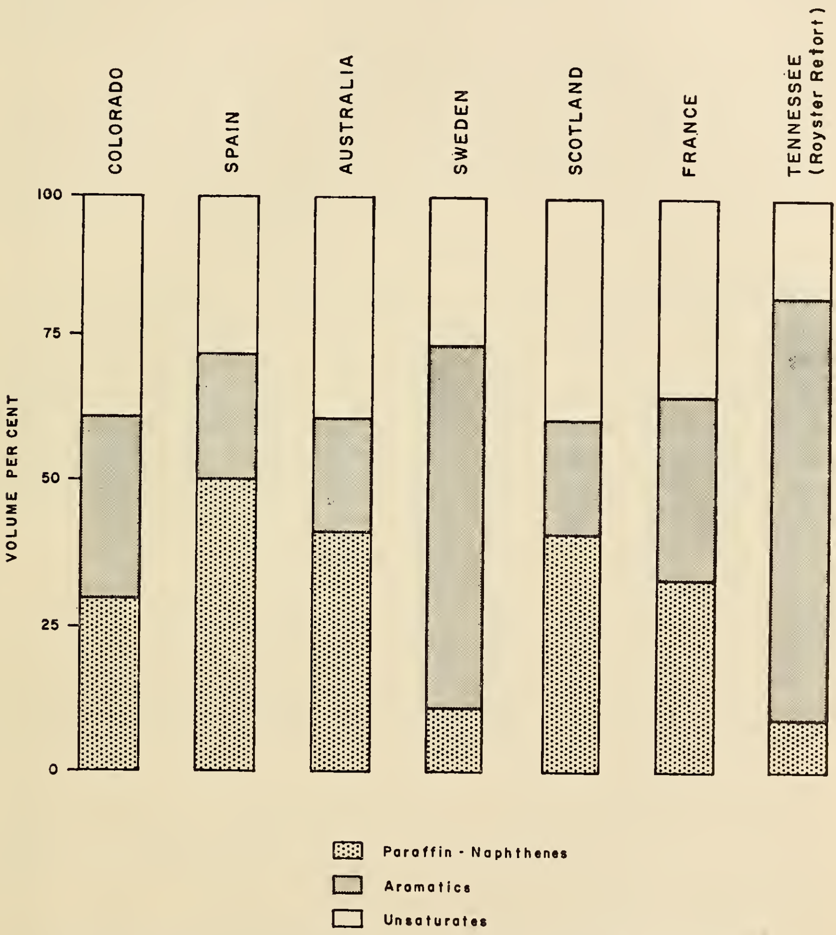


FIG. 3. Hydrocarbon distribution of $<315°C$ distillates of oil shales.

For the reasons given above, much of the compositional data of shale oils in the voluminous literature on this subject are difficult to compare. However, the studies that have been made using the same retorting method indicate that the distribution of molecular weights and types varies appreciably depending upon the source of the shale, as shown in Figs. 2 and 3 (Dineen, 1954). Although there is some variation in the distribution of molecular weights, there are quite marked differences in distribution of molecular types in the 315°C distillates. In Fig. 3 the aromatic contents of the Swedish and Tennessee shale oil distillates are much higher than those of other samples. The high aromatic content of these two oils may be indicative of a coaly type of kerogen, in contrast to the "algal", non-coaly type of kerogen in the Scottish, Australian, and Colorado samples.

Only a limited amount of work has been done in the identification of the non-hydrocarbon constituents of shale oil. Nitrogen bases of various types have been identified in Green River, Fushun, Estonian, and Midlothian shale oils (reviewed by Prien, 1950). However, there is some question as to whether these compounds are representative of the kerogen or are the result of the combination of cracked products and ammonia.

Various oxygenated compounds including phenols, cresols, and xylenols have been identified in Green River, Estonian, and Midlothian shale oil fractions (Prien, 1950). Raudsepp (1954) found the two isomeric naphthols in distillation fractions from Baltic shale (Kukersite?) oil. Aarna (1955) notes that phenols appear even at pyrolysis temperatures as low as 300°C, but is uncertain as to their origin.

It is recognized that theories on kerogen structure based on the composition of ordinary shale oil are complicated by secondary cracking, dehydrogenation and polymerization of the primary reaction products during pyrolysis. In view of this a few attempts have been made to pyrolyze kerogens under vacuum, thus removing the initial reaction products from the heated zone as soon as they are formed. Although several samples have been examined, the products have been only incompletely characterized (Blackburn, 1924; Luts, 1934; McKee and Goodwin, 1923).

Thermal solution, which may be regarded as a modification of dry distillation methods, consists of heating the ground rock in a solvent at high temperatures (385°–450°C) and pressures. Various authors have reported yields of soluble products as high as 96% of the original organic matter (D'yakova, 1944; Thorne *et al.*, 1950). Decalin appears to be one of the better solvents since substantial conversion to soluble products can be obtained with it at temperatures in the 200°C region (Schackenberg and Prien, 1953).

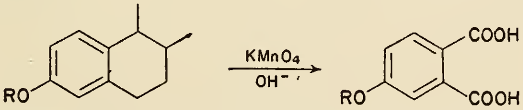
Individual substances that have been identified in thermal solution products of Green River oil shale include cresols, xylenols and higher homologues, unsaturated disulfides, benzofuran, and pyridines and alkyl-substituted pyridines (Thorne *et al.*, 1950).

The results of vacuum distillation and thermal solution studies suggest them as possible methods of structure elucidation. Little or no work, however, has been done on relatively pure kerogen samples, which would appear to offer some advantages in the size of equipment required, and the elimination of absorption of reaction products on clay particles. Possible effects caused by the presence of the inorganic substances themselves would also be eliminated.

Degradation with hydriodic acid and other agents. A new method for the degradation of carbonaceous substance under relatively mild conditions has been published recently by Raudsepp (1954). The method consists of reacting the concentrated kerogen sample with fuming hydrogen iodide at 175°–200°C. The extent of the reaction can be determined by measuring the amount of free iodine produced. With Estonian Kukersite the kerogen was completely broken down into soluble low-molecular-weight compounds. The site of degradation is thought to be oxygen bonds (either ester or ether) analogous to the action of hydriodic acid on methoxyl-containing compounds. From the analysis of the products Raudsepp (1954) interprets the structure of the original kerogen molecule as follows: hydrocarbons with oxygen bridges (ether or ester); elementary units or aromatic nuclei connected by aliphatic chains; and each ring nucleus containing from thirteen to seventeen carbon atoms and phenolic ether groups.

In a modification of the above procedure, Aarna and Lippmaa (1957a) decomposed a kerogen concentrate of Estonian oil shale with aluminum bromide at 100°C. The results were interpreted as indicating the presence of phenolic structures in the kerogen.

Various authors' interpretations of the structure of Estonian oil shale kerogen are conflicting. Kogerman (1938) noted that although considerable quantities of phenols are formed on pyrolysis, the absence of benzenoid acids in the permanganate oxidation products indicates that aromatic structures are absent. However, Raudsepp (1954), and Aarna and Lippmaa (1957a) found definite evidence of aromatic hydroxyl compounds in cleavage products. It should be pointed out that in the presence of alkaline permanganate any aromatic nucleus containing an oxygen function would yield an oxobenzenecarboxylic acid instead of a benzenoid acid:



No benzenoid acids would be obtained from oxygenated aromatic compounds under these conditions. The only possible interpretation consistent with the facts is that some aromatic rings are present in Estonian oil shale kerogen, but most, if not all, have phenolic or ether–oxygen substituents.

Because of the rather low temperatures involved, the hydrogen bromide degradation reaction or its modifications appear to be worth further investigation. It would be of great interest to obtain comparative data on other kerogen samples as well as coals, lignites, peats, and lignin. This reaction does not appear to have been explored to any extent in the coal series.

Functional group analysis. This method is recognizable as a valuable supplement to degradation methods in that it furnishes information concerning the peripheral groups in the molecules. While it has been extensively used in coals, there are few reports of its use for kerogens. Semenov *et al.* (1955) detected two types (light and dark) of kerogen in Baltic shales. The light kerogen type contained about 1.3% of hydroxyl groups and the dark, about 1.6%. These values would correspond to a fairly high rank coal (van Krevelen and Schuyer, 1957). The carbonyl contents of the two types of kerogen were 0.3 and 1.3%. Considerable fluctuation in this value has also been found in coals (van Krevelen and Schuyer, 1957).

Recently it has been observed that about 42% of the oxygen in coals appears to be present as acetylatable hydroxyl groups regardless of rank (Mazumdar *et al.*, 1956; Wyss, 1956). While this work needs additional confirmation, it offers possibilities in estimating the relative proportions of coal-type and non-coaly type kerogens in the same rock.

Aarna and Lippmaa (1957b) recently published experiments that purport to show the aromatic nature of kerogen. The kerogen concentrate from an Estonian oil shale (Kukersite?) was diazotized, methylolated (concentrated hydrochloric acid and *para*formaldehyde), and treated with mercuric acetate. These results of the three methods indicated that between 4 and 17% of the carbon in kerogen is in aromatic rings.

Analyses for other types of functional groups appear not to have been made. It would be of interest to determine the methoxyl content of kerogens in view of the possible origin of one type of kerogen from lignin. The methoxyl content of coal has been shown to decrease with increasing rank, becoming practically negligible at the subbituminous stage. Carboxyl group determinations also would be of value, since these groups are known to occur in brown coals and lignites but not in higher rank coals.

Classification of Kerogen

Classification schemes for kerogen that have been published are generally based on the petrography of the rock and on the organic carbon content. In theory, classification methods based on these criteria have definite limitations. The mineral composition of a rock is dependent, to some extent, on the source material (i.e. on the nature of the rock that is weathered to form the clastic particles brought into the sediments). Thus, a part of the rock mineralogy has no connection with the environment or the forms of life that enter into the sediment. The organic content of a rock also is partially independent of the environment of deposition, since it is largely determined by the relative depositional rates of the organic and inorganic matter. These rates are controlled by a number of factors other than those related to environment.

A more rational classification of kerogen would be based on the *type* of organic matter, which reflects the original life or environment of deposition. The proposed scheme is based on the carbon, hydrogen, and oxygen composition of the kerogen. In Fig. 4, the compositional data of the kerogens listed in Table 3 are plotted on a triangular diagram. Only the upper part of the triangle is shown, but the sum of the C, H, and O coordinates of a particular point always total one hundred. Although different in appearance, the triangular diagram is fundamentally identical to the tetragon adopted by Ralston (1915) for coals.*

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* Since triangular coordinate paper is now readily available, there is no longer any need to use the less familiar four-sided, or Ralston diagram.

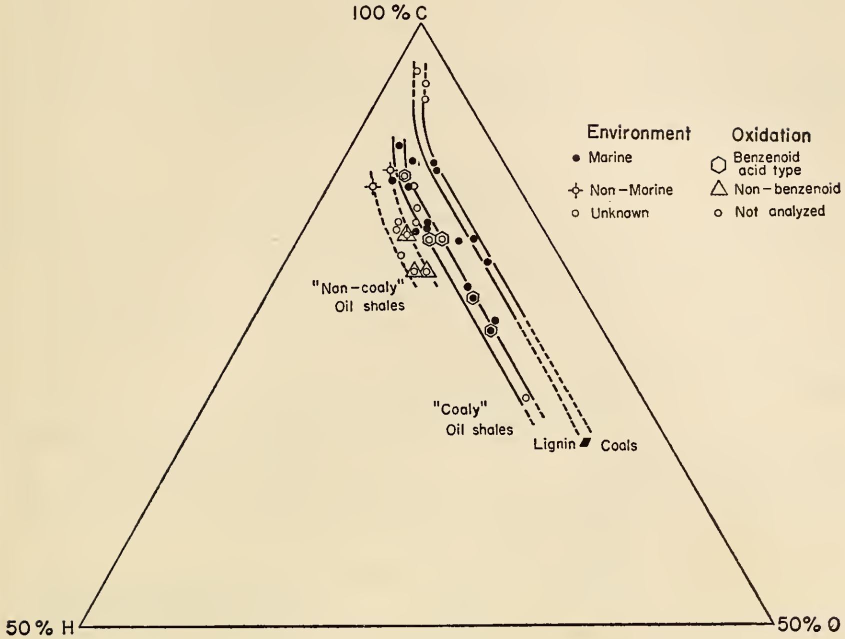

FIG. 4. Kerogen environment and composition.

Wherever possible, the generalized environments of deposition of the rocks gathered from various sources in the literature (summarized in Table 8) are indicated on the triangular diagram. Also included are the results obtained on the seven kerogen samples in which the presence or absence of benzenoid acids in the permanganate oxidation products has been determined (Table 6). Points enclosed by hexagons indicate that various benzenoid acids were identified in the oxidation products, whereas triangles denote the absence of benzenoid acids.

The main features of the diagram are the three bands entitled "coals", "non-coaly oil shales", and "coaly oil shales". Nearly all of the kerogen samples fall within the limits described by these bands.

The coal band, which is adopted from published graphs, (Ralston, 1915; Seyler, 1950) encloses the carbon, hydrogen and oxygen contents of a large majority of normal or bright coals in various degrees of metamorphism or maturation. None of the oil shales fall within this band. However, the kerogens isolated from four marine rocks lie within the band suggesting a close compositional relationship to coals. The environment in which these four rocks were deposited (Table 8) generally appears to be near-shore marine. In two of the samples (Cherokee and Wilcox Shales) remnants of land-derived plants were abundant, and interbedded coals are quite common in these two formations.

Most authorities now agree that the organic precursor of the bright or normal coal constituents is lignin, which acts as a cell binder in vascular plants. The fact that the straight portion of the coal band can be extended (as shown by broken lines) to the composition of lignin (Adler, 1957) strongly suggests that this is the case. By analogy, the composition of the coaly-type kerogen appears to be dominantly lignin-like material that has

TABLE 8

Petrographic Composition and Environment of Deposition of Kerogen-Bearing Formations

Name	Microscopic Appearance	Environment
	Coaly kerogen	
Cherokee sh.	Abundant land plant spores, tissue fragments (Evitt, 1957)	Marine; near-shore (Evitt, 1957)
Frontier sh.		Generally marine (Reeside, 1957; Young, 1951)
Madison dolo.	Tiny brown clumps, unrecognizable organic matter (Evitt, 1957)	Marine, shallow (Hall, 1958)
Wilcox sh.	Vascular plant fragments (Forsman, 1953)	Deltaic, littoral, lagoonal to swamp. (Culbertson, 1940)
Caney sh.	Amorphous, brown, rare spores and cysts, some amber-colored material. (Evitt, 1957)	Marine (Schuchert, 1943).
Ste. Genevieve ls.	Tiny brown clumps of unrecognizable organic matter, Rare tissue fragments. (Evitt, 1957)	Generally marine, shallow (Williams, 1957)
	"Coaly" oil shale type	
Morrison sh.	Little identifiable; rare, well-preserved spores, hystrichospherids, dinoflagellates. (Evitt, 1957)	Continental to marine; this sample near-shore marine. (Evitt, 1957)
Um-Barek sh.	No spores or algae (Gil-Av, *et al.*, 1954)	Marine (Gil-Av *et al.*, 1954)
Monterey sh.		Marine (Natland, 1957)
Traverse ls.	Mostly disaggregated tissues and spores (Evitt, 1957)	Marine, shallow, reefal (Cooper, 1957)
La Luna ls.		Marine (Ladd, 1957)
Kimmeridge sh.		Prob. marine; Interbedded with marine shells (Conacher, (1938)
Ermelo sh.	Largely unidentifiable, some algal remains; rest is dark (Himus, 1950)	
Lothian sh.	Largely unidentifiable, thought to be algal; occ. spores, macerated vegetal matter, pyrite casts (Greensmith, 1957)	Uncertain (Greensmith, 1957

TABLE 8—*continued*

Name	Microscopic Appearance	Environment
	"Algal" (or "spore") oil shale type	
Kukersite	Abundant well-preserved algal bodies (*Gloeocapsomorpha*) (Luts, 1938)	Marine (?) (Luts, 1938)
Duvernay sh.	Amorphous; rare hystrichospherids, chitinozoa (?) (Evitt, 1957)	Marine, algal reefs to east. (Evitt, 1957)
Torbanite, Australia	Unidentifiable resins; thought to be algal remains similar to *Botryococcus Braunii* (Dulhunty, 1943)	Small, fresh-water lakes, algal, from backwaters of marshes (Dulhunty, 1943)
Green River sh.	Golden brown, largely unidentifiable. Rare pollen (Evitt, 1957)	Large, salty lake; nonmarine, tropical or subtropical climate (Cockerell, 1925)
Tasmanite	Spore cases (Conacher, 1938)	Marine (?) (Contains marine shells); coastal (Conacher, 1938)

undergone varying degrees of chemical maturation (loss of oxygen and cyclization) as have coals.

The "non-coaly oil shale" band appears to lie more or less parallel to, and considerably to the left of, the coal band. The kerogens in this category, which have higher hydrogen–carbon ratios than the coaly type, are from rocks deposited under both marine and non-marine conditions (Table 8). With the exception of tasmanite, whose dominant constituent is spore cases, most of the kerogens in this type are believed to be algal in origin. Three kerogen samples in this group have been oxidized by alkaline permanganate, but no benzenoid acids could be identified in the products. As discussed above, this and other chemical evidence suggests that in this type of kerogen open-chain structures predominate; some cycloparaffin groups also may be present. If aromatic rings are present, oxygen atoms must be attached to them.

The third band, which lies between the two just described, may be termed the "coaly oil shale" band. Members of this group appear to have properties intermediate between those of the coaly and non-coaly types of kerogens. Of the rocks whose environments of deposition appear to be well established, all were deposited under marine conditions (Table 8). In addition, the five oil shales that yielded benzenoid acids on alkaline permanganate oxidation fall within this group.

The compositional data (Fig. 4) suggest that the coaly-oil shale type of kerogen is made up of mixtures of coaly, lignin-derived material and algal (or spore) remains. Microscopic and chemical evidence on a few kerogens (see section on oxidative degradation) offers strong support to this statement. It may be possible to separate these two types of material by physical methods. The Traverse Limestone, whose kerogen appeared to consist of both spores and plant tissue (Table 8), separated into two fractions during the first acid treatment of the rock (Forsman, 1958). Surprisingly, the fraction that floated had a higher specific gravity than the fraction that sank to the bottom on centrifuging; apparently the separation was caused by differences in the hydrophilic nature of the two fractions. The floating fraction contained almost half as much oxygen and hydrogen as the other fraction. Moreover, this fraction did not yield oil on pyrolysis, whereas the more hydrogen-rich material did (Forsman, 1953). This is in accord with the observations of Down and Himus (1941), who regard the hydrogen-rich or algal portion of the Ermelo kerogen as the main contributor to the shale oil.

Four or five of the kerogens in Fig. 4 appear to have compositions intermediate to the three types just described, indicating that there is a gradiation in the types of kerogen present in rocks. However, although algal oil shales (torbanites) of Australia are often interbedded with coals, the kerogen types change very abruptly in a vertical direction and show little tendency toward intergradation (Dulhunty, 1950).

Properties of kerogen appear to be unrelated to geologic age or type of rock (Forsman and Hunt, 1958). There also is no apparent connection between these properties and depositional environment (marine or non-marine), although only a few kerogens formed under non-marine conditions have been analyzed. The environmental data given in Table 8 are too general to show relationships to other factors such as proximity to shore line. Much more detailed stratigraphic and paleontological studies are needed to establish relationships between composition and environment.

Maturation or metamorphism of both the coaly and coaly oil shale-type of kerogen is indicated from the fact that the data points in Fig. 4 are fairly well distributed along their respective bands. Evidence for maturation in the "non-coaly oil shale" type of kerogen, however, is inconclusive. Inasmuch as the chemical constitution of this type of substance is entirely different from that of coal, the maturation mechanisms in these two series would be expected to be different. It is possible that in the mixed, or coaly oil shale, type of kerogen, the lignous fraction undergoes chemical reactions (such as loss of oxygen and cyclization), while the algal portion of the kerogen remains essentially unchanged.

The compositions of two kerogens from metamorphosed rocks (Table 3) lie near the top of the triangular diagram in the metamorphosed (anthracite) coal region. X-ray difraction spectra definitely indicated that graphite-like material was present in one of these samples (Forsman and Hunt, 1958). The very high carbon content of the kerogens found in metamorphosed rock is additional evidence for change of rank in kerogen.

The analysis of anthraxolite (the uppermost circle) is especially interesting. Various origins, including crude oil and asphalt, have been proposed for this type of material. One possibility, however, is that anthraxolite was originally a very rich oil shale (such as that found at Mangaroo, New

South Wales) that has been strongly coalified through the action of metamorphic forces on the surrounding rocks.

Summary

The nature of kerogen—There is evidence that at least two, and possibly three types of kerogen occur in sedimentary rocks. These substances are the residues of once living matter and have resisted destruction by chemical and biochemical forces during geologic time. However, there is evidence that kerogen changes in rank as do coals, tending toward pure carbon as the end product.

These great classes of kerogens appear to be entirely different structurally. The first type, which has been called the coaly type, appears to be similar to coal in all properties. Because of this similarity, predictions about the nature of this type can be based, with a fair margin of safety, on the wealth of information on coals that has been gathered by innumerable investigators. There are strong indications that the coal-type kerogen is a macro-molecule consisting of condensed aromatic rings interconnected by ether, alkoxy, and perhaps sulfur bridges. Also attached to the aromatic nuclei are hydroxyl groups, methoxyl groups, and perhaps esterified carboxyl groups. Much more chemical study is required on this type of kerogen with regard to both the nucleus of the kerogen molecule and the peripheral groups.

The second ("non-coaly") type of kerogen appears to have a more nearly open chain structure, with some cycloparaffin or mononuclear aromatic rings attached. Oxygen, and possibly nitrogen and sulfur atoms, may act as connecting links between rings. Very little of a definite nature is known about how the atoms are arranged in the molecule. As discussed earlier, both aromatic and non-aromatic structures have been ascribed to the Estonian oil shale kerogen.

A third class of kerogen, the "coaly oil shale" type, has properties intermediate between the other two. In some cases, this type may be merely a physical mixture of the "coaly" and "algal" types of kerogen. In others, the kerogen may consist of molecules with alternately condensed and open chain structures.

Possible origins—Because of our lack of knowledge of the constitution of kerogen, any statements regarding the origin or precursors of kerogen must necessarily be speculative. It seems fairly safe to assume that kerogen represents the resistant portions of organisms that were deposited with the sediments. Unfortunately, little is known as to the chemical nature of the most resistant compounds in various orders of plant and animal life. The one exception is lignin. Of the more abundant constituents of woody plants, lignin is by far the most resistant to chemical and biochemical agencies. Most authorities now agree that lignin is the precursor of the major portion of coal substance. However, the structure of lignin has not been completely determined, although most of its structural elements are now known (Adler, 1957).

It might be reasoned that if coal is derived from lignin-containing plants, then the coaly type kerogen must be also. Whether these lignins were brought into the sediments as particulate or dissolved organic matter by streams is an open question. Virtually nothing is known about the true lignin content of either lacustrine or marine plants or of sediments. The few data that are reported for aquatic plants and sediments are based on the rather unsatisfactory method of expressing the "lignin" content as the organic matter insoluble in 70% sulfuric acid. If it is true, as has been suggested by some authors, that lignin is formed through biochemical agencies from cellulose, the coal-type kerogen could even have originated from micro-organisms that contain cellulose but no lignin.

From a chemical standpoint alone, it would be difficult to state the origin of non-coal type kerogens. In certain torbanites, however, a careful microscopic examination indicates that the bulk of the kerogen is made up of algal (or spore) remains. In many cases, however, the kerogen consists of an unresolvable mass. This organic matter may represent the macerated, organic-rich debris (sapropel) that forms as bottom deposits in shallow, stagnant, nutrient-rich waters.

Other Extensions of Kerogen Studies

Thus far, studies of kerogen have been restricted to a relatively few isolated cases scattered over the world and through geologic time. Nothing is known as to the lateral or vertical variations that might exist within a particular bed. There are a number of formations, such as the Devonian Chattanooga Shale of the United States, the Cretaceous La Luna Limestone of South America, or the Colorado Shale of Canada, where such studies could be made. It would be interesting, for example, to see whether the composition and other properties of kerogen show large local variations or show wide-spread uniformity. More definite evidence for or against the maturation of kerogen could be obtained by making side-by-side comparisons of kerogens and coals starting in an area of a relatively low degree of metamorphism and proceeding towards one of a higher degree.

Further studies from the standpoint of the origin of petroleum could be quite illuminating. It is possible that the coaly type of kerogen represents organisms which did not play a major role in the formation of oil, whereas those that formed the non-coaly types may also have been the precursors of petroleum. If this were the case, methods for estimating the relative amounts of the two types of kerogen in a rock would be useful in petroleum source rock studies.

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CHAPTER 6

GEOCHEMISTRY OF COAL

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Introduction

COAL, mineral oil, and kerogen are the most important reservoirs of carbon in the world. At present coal and oil are not only major sources of energy but also principal raw materials for the chemical and metallurgical industries. Coal resources located at workable depths are still enormous; some 10^{12} tons. In this chapter are discussed the geological, physical, chemical, and technological aspects of coal. Following a discussion of the geological environment of coal deposition and a description of coal as an organic rock, the progenitors and genesis of coal will be considered. After that, its physical and chemical properties will be described and explained on the basis of structure and composition. The chapter also includes a brief survey of coal utilization and classification.

Geological Environment of Coal Deposition†

The formation of coal seams—Geological history has known two great eras of coal formation. The first is sometimes called the *Anthracolithicum*, which extends from the Lower Carboniferous to the Permian. It is to the tremendous development of the coal deposits during this era—especially in the Carboniferous—that North America and Europe owe their abundant coal resources. Carboniferous rocks were, mainly on the northern hemisphere, laid down in a wide belt. The depth of these formations was enormous; that of the Upper Carboniferous alone must have exceeded three miles. It is probable, therefore, that during this period uninterrupted swamps, spread over vast areas, must have gone through a process of steady subsidence, which was largely balanced by sedimentation. A striking example of such an extensive sunken area, called a geosyncline, is the Pittsburgh seam of the eastern part of the United States, which can be mined over an area of 8000 square miles. In many places the productive Upper Carboniferous has disappeared owing to earth movements; one part has sunk to great depths, while another part has become eroded. These effects account for the considerable differences in coal deposits through the Carboniferous belt. Total coal deposits constitute no more than about 2% of the Carboniferous sediments, so that coal is rather rare even within the Carboniferous. Generally speaking, the Paleozoic coal-forming process started in the northwest (North America) and gradually spread towards the southeast. This is confirmed by the fact that the coal strata in Siberia, Eastern Asia and Australia were laid down during the Permian.

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† For more extensive discussion reference may be made to the following monographs: Potonié, 1910; Stopes and Wheeler, 1918; Gothan and Franke, 1929; Stadnikov, 1930; Raistrick and Marshall, 1939; Moore, 1940.

The second era of coal formation—one of less qualitative importance than the Carboniferous—commenced in the Late Cretaceous and reached its peak in the Tertiary. Nearly all lignites and brown coals date back to this period.* This coal-forming process, too, had its start in the northwestern part of the northern hemisphere: the tremendous coal fields in the western part of North America, extending from Utah into Alaska, were accumulated during the Cretaceous. In Europe, the lignite fields in the south of France, and in Central Europe were developed during the Upper Cretaceous and the Eocene. The bulk of the lignite formations, along with the Tertiary coals of Japan, Indonesia and Patagonia, were laid down in the Miocene.

To explain the formation of the vast and thick peat beds, which subsequently were transformed into coal, it has to be assumed that the geosynclines did not sink at a constant rate but that periods of slower subsidence alternated with periods of more rapid sinking. It is obvious that when the rate of subsidence slackens it will be exceeded by sedimentation. As a result, the lagoons become shallow, favoring the growth of aquatic plants so that extensive swamps can form. Apart from a few rivers traversing the swamp, the water is nearly stagnant and plant debris continues to accumulate. In a subsequent period trees develop on this weak boggy soil. Roots of these Carboniferous trees (stigmaria) are found in nearly all coal seams, which may be regarded as a clear proof that the coal has generally been formed *in situ* (autochthonous formation). The genesis of most coal deposits goes back to a living peat bog such as is still found in several places. This vegetation continues to grow for many generations; the plant material settles on the swamp bottom and is converted into peat by microbiological attack. The accumulation of such peat continues until the rate of subsidence of the geosyncline increases again. For some time the swamp vegetation persists in spite of the altered conditions, especially those plant types that are capable of growing in deeper waters. Finally, however, the swamp is submerged and covered by sedimentary deposits and a future coal seam has formed. Afterwards the cycle may be repeated, and this sequence accounts for the formation of the numerous coal seams in the course of hundreds of thousands of years.

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* It is remarkable, however, that the brown coal of the Moscow Basin was formed during the Lower Carboniferous.

The development outlined above may be considered to have been the normal coal-forming process: the peat formation beginning under fairly dry conditions and ceasing when the area was flooded. Yet, this has not been the case everywhere, and some coal strata owe their existence to the silting up of deeper waters, where peat formation consequently started under very moist conditions. The cessation of the peat-forming process, however, must in nearly all cases be attributed to submergence.

Besides the subsidence of a whole region (geosynclinal subsidence), the settling of the older underlying strata also plays an important part. A marked degree of settling can be noted especially in the case of buried peat beds. This is a possible explanation for the wide differences observed in the individual development of sedimentary layers and coal strata.

Following the formation of peat, the strata went through a period of far-reaching diagenetic and tectonic influences. The following review of the changes thus brought about is restricted to Carboniferous coal strata because the history of these coals is much more varied than that of the Tertiary coals.

Assuming that the buried peat-bearing strata initially extended in a horizontal plane during the last part of the Carboniferous, and therefore "shortly" after their formation, the deeply buried strata were in many places exposed to a process of folding (orogenesis) in which a large number of major and minor faults developed. Later, tectonic forces acting upon the earth's crust were no longer capable of refolding the stiffened Carboniferous strata. In this period, therefore, great and long faults developed along which sections of the crust were raised or depressed, a movement not unlike that of ice floes.

From the time the peat beds became buried under sedimentary accumulations and started to sink more and more deeply into the earth's crust, their chemical composition began to change.

When water-logged peat is covered by an impervious sediment, there arises a situation that bears much resemblance to the conditions prevailing in an autoclave: the peat is slowly altered, at the outset under water-logged conditions, by chemical reactions (metamorphosis). Gradually the carbon content of the fossil plant material increases; this chemical change is called coalification. In the light of the data that have become available, it is understandable that there must exist a genetic relationship in the peat–lignite–bituminous–anthracite series, known as the coalification series.

The causes of coalification—As stated above, biochemical factors play an important role in the very first stage of the coalification process. Microbiological decomposition, however, can only continue as long as fungi and bacteria are capable of participating in the attack on the material. Fungi do not occur beyond a depth of about 40 cm and the formation of lignite, therefore, cannot have been influenced by the action of these organisms. The effect of bacterial action also decreases with depth, so that at great depths extensive bacterial conversion is impossible. Thus it follows that geophysical factors must have been effective in coalification beyond the lignite stage.

This view has not been shared by all investigators. Taylor (1926, 1927, 1928) considered bacterial decomposition to have been the main agency in the formation of the various types of coal. It was suggested that decomposition by bacteria depends on the pH and the redox potential of the peat bed, and Taylor proposed that under aerobic conditions peat can be transformed only into brown coal. Furthermore, when the peat deposits are buried under a clay cover, which through an ion-exchange process with salt water is converted into sodium aluminium silicate, conditions become favorable for the formation of higher rank coal because such cover is not only impervious to gases (so that conditions are kept strictly anaerobic) but also produces a slightly alkaline medium. By this hypothesis, therefore, the metamorphosis of a peat deposit is more or less dependent on the character of the sedimentary cover.

Fuchs (1946, 1951, 1952) even went further than this, considering bacteria to have been the only significant agency in the decomposition process. Fuchs postulated that redox potential depends practically completely upon the depth to which the material is submerged, and that redox potential, which changes with depth, is stabilized by the action of microorganisms.

Time alone seems to have hardly any influence on coalification beyond the lignite stage. Mention has already been made of the brown coal of the Moscow Basin which, although it was deposited during Lower Carboniferous time, has not been coalified to a higher rank; there is evidence to show that this brown coal was never buried to a great depth and has not been exposed to tectonic influences.

It would be inconsistent with thermodynamics to regard overburden alone as the cause of coalification. Pressure has, however, had an effect upon compactness and porosity, and hence on the moisture content, of the coal.

It is not clear that tectonic pressure has not been a major factor in coalification, as is shown by the lack of correlation between the coal rank and the intensity of the crustal movements. Investigations in the Ruhr and South-Limburg basins have shown that coalification was more or less completed before the start of the folding process (Teichmüller, 1951). This movement having occurred at the end of the Carboniferous, it follows that coalification must have taken place during this era, i.e. within a period of about twenty-five million years. A point in favor of this view is that the lines connecting points of equal rank (isovols) exhibit the same folds as the strata.

In the opinion of the majority of the investigators, this leaves only the influence of temperature as a possible explanation of metamorphosis. As mentioned before, the Carboniferous strata must once have been overlain by a very thick sedimentary cover. The temperature to which the strata were exposed depends upon the temperature gradient, as a rule, about

1°C per 100 ft. Accordingly, temperatures lower than about 200°C would have been effective in the formation of anthracite. However, the geothermal gradient is not constant, and local magma pockets under the earth's crust may have exerted a strong regional influence leading to higher temperatures.

Contact metamorphism resulting from volcanic action has such localized significance that it cannot be considered to have had any appreciable effect on coalification.

Coal-forming plants—Generally speaking, no macroscopically recognizable plant residues are found in coal; the underlying, and occasionally also the overlying deposits, on the other hand, do contain well-preserved remains and indications of ancient plant life (see Gothan and Franke, 1929; Raistrich and Marshall, 1939).

The fossils found under the coal beds consist of roots that accumulated in root or stigmaria banks. The roof layers to a height of a few meters frequently contain a plant bank of shaly composition in which plant impressions, sometimes of great clarity, can be distinguished.

Carboniferous flora may be divided into four major groups: the Articulatae (horse tails), the lepidophytae (club mosses), the Pteridophyllae (ferns and their allies), and the Cordaites (Gymnospermeae). Of the Articulatae only the Calamites grew in the form of trees. They had a long, transversely ribbed and jointed stem, with small leaves or whorls of sparse foliage growing from the nodes. These trees grew in swamps where they played the same part as the reeds of our times (Fig.1).

The most important representatives of the Lepidophytae were the Lepidodendrons and the Sigillaria. The Lepidophytae were also high trees, which grew in a somewhat drier habitat than the Calamites. They had a typical bark showing regular patterns of large scars caused by the loss of leaves during secondary thickening of the bark. The leaf scars of the Lepidodendrons were arranged along diagonal, those of the Sigillaria along vertical lines. Just as in the case of the Calamites, these trees gradually developed a hollow pith; they had a slender trunk crowned by a plume of foliage (Fig.2).

The Pteridophyllae included both the ferns proper (Pteridophytes) and the seed ferns (Pteridospermae). These ferns, which grew in a profuse variation of types, were the finest plant species existing during the Carboniferous period. They grew in a relatively dry environment.

The Cordaites, finally, were a somewhat conspicuous species among the Carboniferous flora; these trees had a high stem with long narrow leaves showing some resemblance to palm leaves. As these plants were even less water-loving than the former, it must be concluded that they did not occur in swampy grounds, but on the slopes of the hinterland.

From the foregoing it will be clear that the character of the vegetation may furnish some information on the conditions under which humification, the initial stage of coalification, must have occurred.

Plant spores are of particular importance to the study and identification of coal strata. Spores often constitute an important component of the coal and occur in practically all coal seams. Even though numerous macro- and micro-spores cannot be traced back to a given plant species, the study of spores has been of great significance for the identification of the seams. The type and quantity of a given spore, or accumulation of spores, in a coal seam has frequently proved to be an unambiguous means of identification, as well as a typical characteristic of the ecological conditions prevailing in primeval forest swamps.

Carboniferous forests must have grown in areas that were almost completely flat and where vegetation in the forests did not vary to any appreciable extent. This is indicated by the existence of plant banks which, over areas of several square miles, consist of the same small number of plant types to the near exclusion of other forms of vegetable life. Mixed forests hardly occurred and the forests, therefore, must have been rather monotonous in appearance. In other regions, fern fields were predominant over vast tracts of land. In the latter case it might be more correct to speak of a peat swamp rather than of a forest swamp.

The Carboniferous climate was apparently very rainy, while the absence of annual rings in the tree trunks indicates that the temperature was rather constant. It is probable, therefore, that the climate had a subtropical character.

Coal as an Organic Rock*

Aspects of coal petrology—Coal is an organic rock. Just as an inorganic rock is composed of petrological components known as minerals, coal also consists of petrological components that are called *macerals* (Stopes, 1919, 1935). The main point in which coal differs from an inorganic rock is that its composition is not constant but varies according to the position or rank of the coal in the coal series.

Coal components, or macerals, can only be identified microscopically (Fig. 3). These examinations can be made by several techniques; the two principal ones, which more or less complement each other, are discussed below. The first method, which was developed mainly in Great Britain and the United States (Lomax, Stopes, Hickling, Marshall, Thiessen, Cady, Sprunk, Schopf, Parks, Cross, Kosanke, Spackman) uses thin sections and transmitted light (Cady, 1945). Examinations by the other technique are made under (Stach, 1949) the metallurgical microscope using polished sections and reflected light. This method was entirely developed in Europe (Winter, Stach, Seyler, Duparque, Jongmans, Legraye, Hoffmann, Kühlwein, Abramski, Mantel, Mackowsky, Teichmüller). A third and recent method which was used for the first time by Hsieh, and perfected by Hacquébard and Teichmüller, is the examination of polished thin sections; this method may be considered as a combination of the former two techniques (Hacquébard, 1950; Teichmüller and Parks, 1956) Methods based on the use of transmitted and reflected light have been highly perfected and each has its own specific advantages and disadvantages. They should, therefore, be considered as complementary methods. Transmitted light clearly reveals color differences between the various components and is ideally suited for examination of components that are truly transparent; reflected light is to be preferred when dealing with the opaque constituents. Polished faces can be prepared of coals of any rank; thin sections of high-rank coal are rather difficult to make.

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* See Stopes and Wheeler, 1918; Legraye, 1932; Stach, 1935; Raistrick and Marshall, 1939; Lowry, 1945; Stach, 1949; Abramski, Mackowsky and Mantel, 1951; Francis, 1954.

The thin section technique offers many advantages for morphological investigations. For quantitative comparative examinations, however, (i.e. of ground coal specimens) the reflection technique is to be preferred. The differences between the two techniques have led to different nomenclatures in the field of coal petrology.

Components or macerals—It has been found that woody tissue is capable of two extreme ways of coalification without loss of morphological structure: to *telinite* or *anthraxylon* on the one hand, and to *fusinite* on the other. Although the woody structure has been preserved in both extreme modifications, telinite is transparent (orange or red) in thin section (except in coal of the highest rank) whereas fusinite is always opaque. The lumens in telinite are always filled with colloidal humic matter or resin; the lumens in fusinite are either empty or filled with mineral constituents. Telinite has a vitrous lustre; fusinite is dull or silky in appearance and is very friable. The transition between the two modifications is called "*semi-fusinite*".

In the course of the coalification process woody tissue may, however, completely lose its structure. The colloidal modification, which is translucent in thin sections, is called *collinite*. This term corresponds with the term *humic matter* (partly with *brown matter*) in the American nomenclature. The other form, completely opaque under transmitted light, is known by the name *micrinite* (*granular* or *massive*) which is identical with *opaque matter* in the American nomenclature. As to the other plant constituents, the resins and waxes (*resinite* and *cerinite*), spore coats (*sporinite*), cuticles (*cutinite*), and fungal sclerotia (*sclerotinite*) can be clearly distinguished.

The macerals and components have been compiled in Table 1, where also the maceral groupings used in Europe and U.S.A. are also given.

In Europe the macerals are classified according to their technological properties:

vitrinite includes the (technologically identical) substances telinite and collinite. On heating, these macerals normally leave a fused coke button as their main product;

exinite includes the remainders of waxy and corky products which, on heating, are largely transformed into gas and tar;

TABLE 1

Survey of Petrologic Components (Macerals) in Coal and their Groupings used in Europe and in U.S.A.

Maceral grouping in Europe	Macerals or components			Maceral grouping (constituents) in U.S.A.
	Name in Europe*	Fig.	Name in U.S.A.†	
Vitrinite	Telinite	3.1	Megascopic anthraxylon ($>500\mu$) Attrital anthraxylon (15–500μ)	Anthraxylon
	Collinite	3.2	Sub-anthraxylon (3–15μ) Humic matter ($<3\mu$) Light brown matter	Translucent Attritus
Exinite	Resinite Cerinite	3.3	Red resins Yellow resins Amorphous wax	
	Sporinite (exinite) Cutinite Suberinite	3.4–3.5 3.6	Spore coats Cuticles Suberin	
	Alginite	3.7	Algal bodies	
Inertinite	Massive micrinite Granular micrinite	3.8 3.9	Dark brown matter Amorphous opaque matter Granular opaque matter	Opaque Attritus
	Sclerotinite Semi-fusinite Fusinite	3.10 3.11 3.12	Fusinized fungal matter Dark semi-fusain Attritac fusain ($<500\mu$) Megascopic fusain ($>500\mu$)	Petrologic Fusain

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* The majority of these names originated with M. C. Stopes (1935) and were adopted by the International Stratigraphical Congresses (1935 and 1951) at Heerlen.

† These names emanated mainly from R. Thiessen (see Cady, 1945); for a survey see J. M. Schopf (1956).

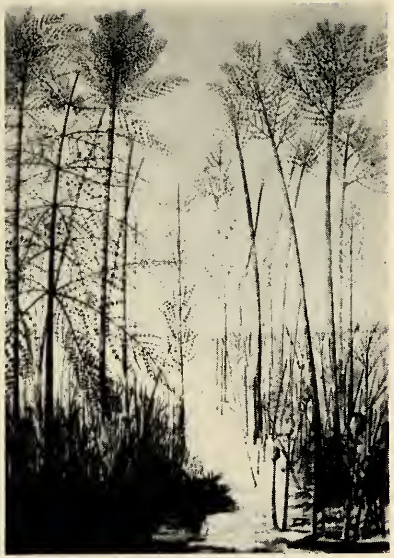

Fig. 1. Reconstruction of a Calamite forest (Museum of Natural History, Stockholm). Typical example of "wet" Carboniferous vegetation.

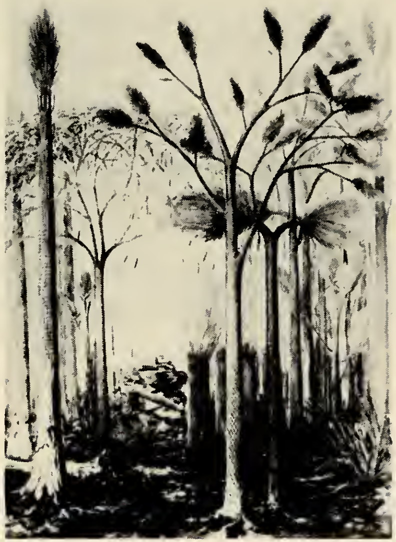

Fig. 2. Reconstruction of Lepidodendron and Sigillaria forest of the Carboniferous period (Museum of Natural History, Stockholm). Note the sparse branching and poorly developed foliage. The picture gives a typical impression of "dry" Carboniferous vegetation.

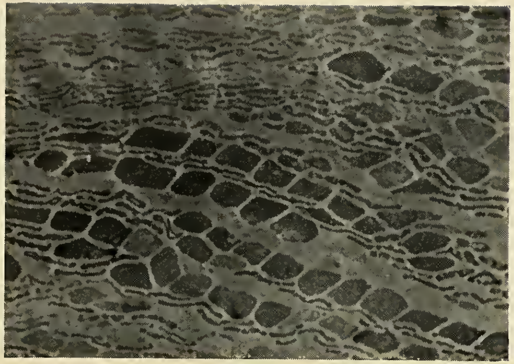

FIG. 3.1. Bright coal essentially composed of vitrinite with woody structure (telinite) (× 400).

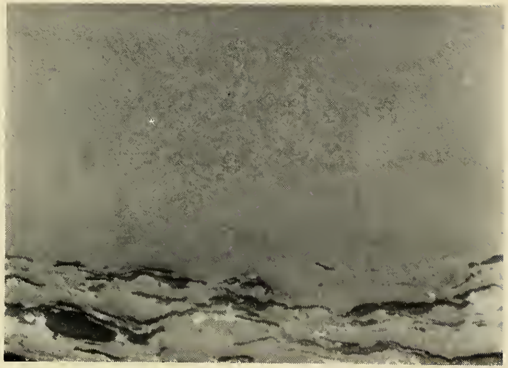

FIG. 3.2. Bright coal with structureless vitrinite as its main component (collinite) (× 400).

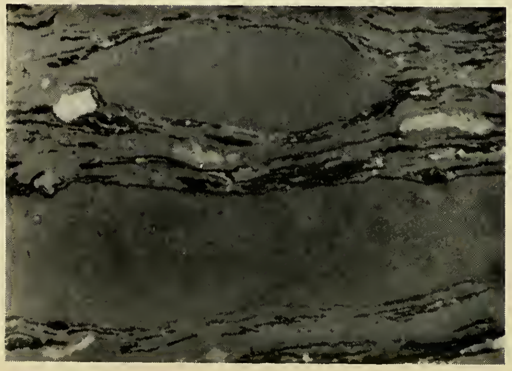

FIG. 3.3. Bright coal with resinite inclusions (× 400). Note the oval shape, which is often observed.

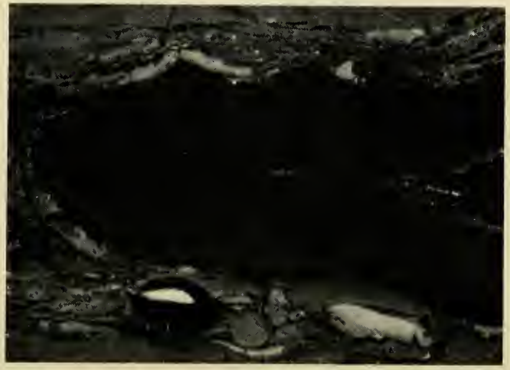

FIG. 3.4. Macrospore (× 400).

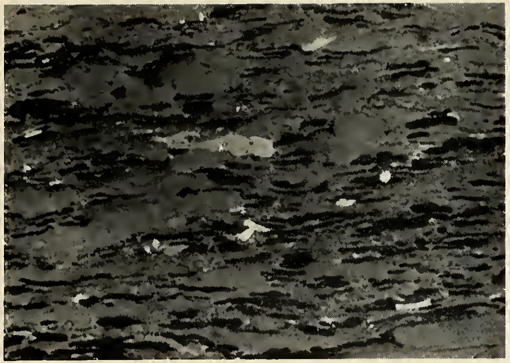

Fig. 3.5. Microspores (× 400).

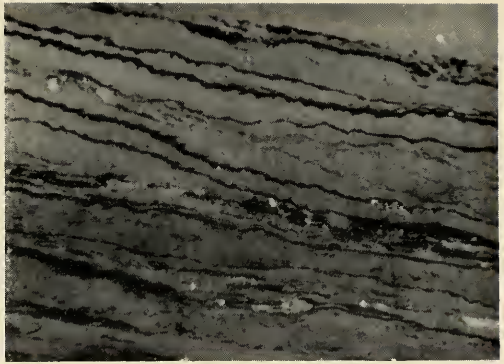

Fig. 3.6. Cuticles (× 400).

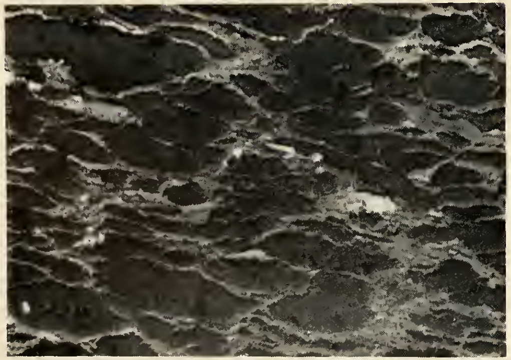

Fig. 3.7. Boghead coal composed essentially of alginite (× 400).

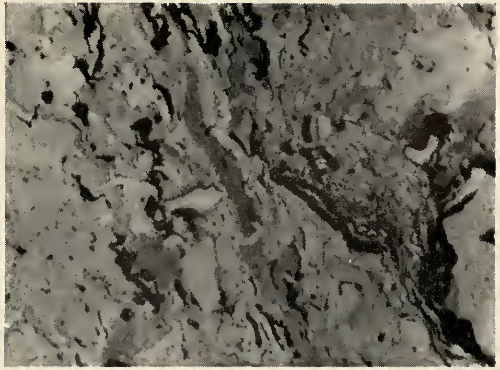

Fig. 3.8. Durain with abundant massice micrinite (× 400).

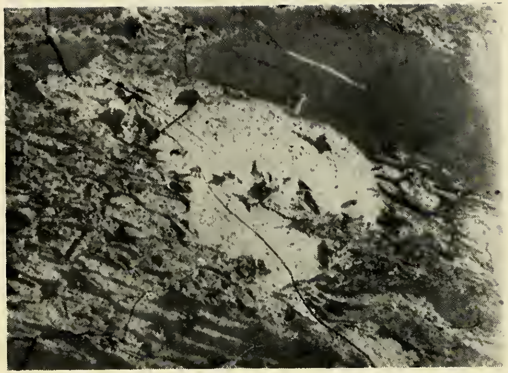

FIG. 3.9. Bright coal showing layers of granular micrinite (× 400).

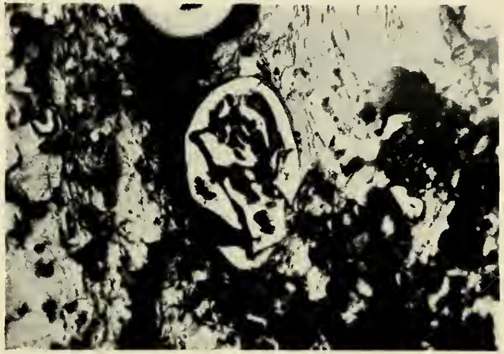

FIG. 3.10. Inclusions of sclerotinite in dull coal (× 200).

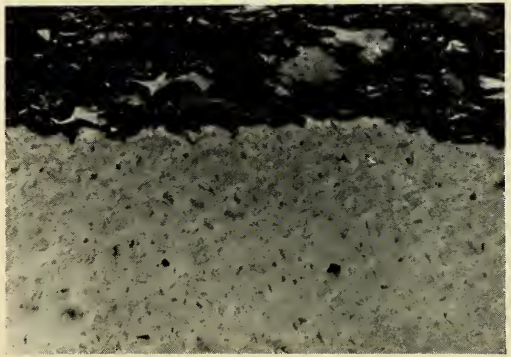

FIG. 3.11. Semi-fusinite (× 400).

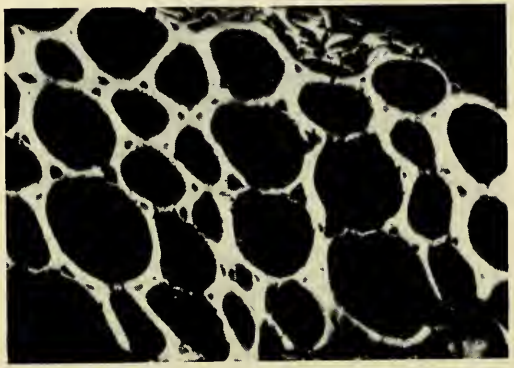

FIG. 3.12. Fusinite (× 400).

inertinite includes all chemical, practically inert, macerals which do not soften or cake on heating and cannot be hydrogenated.

In the U.S.A. the macerals (besides anthraxylon) are classified mainly according to their morphological and optical properties into the following categories: *translucent attritus*, *opaque attritus* and *fusain.*

Rock types—On the basis of the components or macerals, coal is distinguished into various rock types. Coal with over 95% of vitrinite is called *vitrain*, coal containing both vitrinite and exinite is known as *clarain.* Vitrain and clarain form the group of the bright coals. If the coal contains substantially micrinite and exinite (besides smaller additions of other constituents) we speak of *durain* or dull coal. Finally, coal composed mainly of a mixture of fusinite and semi-fusinite is called *fusain.* This nomenclature is based on the original macroscopic classifications by Fayol and Stopes.

The above list of normal coal types may be extended with: *cannel coal* (micrinite with very many microspores), *pseudo-cannel* coal (mainly composed of micrinite and mineral constituents) and *boghead coal* or *torbanite* (alginite and micrinite). These coal types were only formed under special conditions.

It should be pointed out here that the quantitative analysis according to the thin-section and the polished-face methods need not lead to identical results, as can be clearly seen from Fig. 4 (taken from a publication by Teichmüller and Parks, 1956).

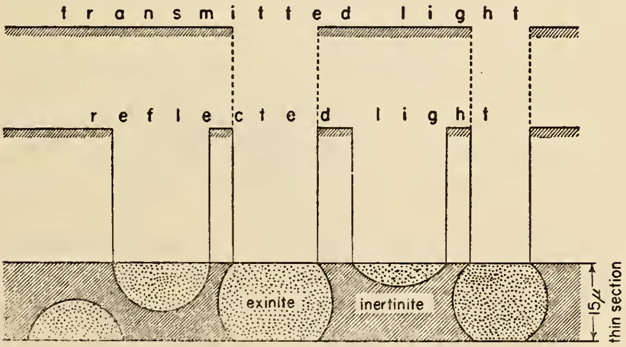

FIG. 4. Explanation of analytical differences in amount of exinite (yellow translucent attritus) and inertinite (opaque matter) observed in transmitted and reflected light.

Genesis of the Various Rock Types and Macerals

It has been shown that woody tissue may be transformed into at least four macerals (telinite, collinite, fusinite, and semi-fusinite) and that micrinite probably also originates in lignified material. Obviously, the differences among the end products resulting from the coalification of similar parent materials has largely arisen from the differences in the conditions under which humification occurred.

It must be assumed that fusain was formed in "very dry" sites. In view of the strong similarity between fusain and charcoal, many investigators believe that forest fires, caused by lightning storms, have been responsible for the formation of fusain. Forest fires must undoubtedly be regarded as one of the possible causes of fusain genesis. Another plausible hypothesis, however, is that fusain may have been produced by a special exothermal microbiological process bearing some resemblance to the spontaneous combustion of hay. Whatever the actual cause has been, it is an irrefutable fact that fusain was coalified, perhaps even carbonized, by a rapid process and under dry conditions.

In considering the genesis of vitrain it is obvious that the lumens are filled with collinite (occasionally with resinite), in contrast to fusain where the lumens are hollow or filled with mineral matter. The frequent concurrence of the macerals fusinite and vitrinite and the existence of transitory gradations between these macerals (semi-fusinite), would suggest that vitrinite was also formed under fairly dry conditions, such as in a swamp where the ground water level was only slightly below the surface. The whole vitrain structure indicates that the woody tissue has gone through a process of mummification. Evidently, the dead plant material sank rapidly into the weak humus soil and became bedded in a medium where water was practically stagnant. The amount of oxygen present in such a medium is so small as to inhibit the growth of anaerobic bacteria. In this toxic environment the material is protected from the influence of the micro-organisms and mummified.

In a true wet swamp the coalification process proceeds along quite different lines. When the surface of the soil is under a sufficient ground water cover, a certain amount of drift may occur and the supply of oxygen is constantly replenished thus preventing the water from becoming acidified. Under these conditions plant debris is destroyed and decomposed to a far higher degree, so that only the more resistant fragments are left. This accounts for the difference between vitrain and durain, the latter consisting in part of highly resistant exinite. Hence, it must be concluded that durain was formed in much wetter sites. Another point in favor of this conclusion is the character of the plant material. Durain is rich in spores formed by the Articulatae, a flora growing in very swampy soils. This vegetation contains less woody tissue than that responsible for the formation of vitrain. Furthermore, durain contains more mineral matter than vitrain, partly of drift origin. The extreme variety of durain, classified as pseudo-cannel, was produced under the wettest conditions. Within the coal seam ordinary durain may, both horizontally and vertically, merge into this rock type.

The most striking features of pseudo-cannel are its homogeneity, its fine texture, and its very dark color. This appearance can only be understood by assuming that pseudo-cannel originates from vegetable mud suspended in free water. In vast swampy areas of the present, pools are also found with black water and with vegetable mud on the bottom. Since the mineral matter of pseudo-cannel contains a much larger proportion of aluminum oxide, it follows that pseudo-cannel is mixed with clay.

The strongest argument advanced by those advocating that pseudo-cannel coal has been formed in open water is the absence of stigmaria banks in pseudo-cannel deposits found in the bottom portion of a seam. This is the more noteworthy because stigmaria banks do appear when the thickness of the pseudo-cannel bank is less than 10 cm. Where the pseudo-cannel bank occurs in the top of the seam, the overlying rock frequently contains fresh water shells.

From this it may be concluded that the differences between the rock types found in normal coal, are due to the variations in "humidity". Whereas fusain and vitrain could develop in relatively dry conditions (forest swamps, "Waldsumpfmoor"), the genesis of clarain required wetter conditions. Durain was produced in a true wet swamp, while pseudo-cannel originated from vegetable mud laid down in open pools ("Faulschlamm") (Potonie, 1910).

This view of coal genesis is in agreement with the hypothesis proposed by the great American geologist David White (1933), who presented his concept in the concise form illustrated in Fig. 5. The composition of the vegetable material is plotted on the abscissa, the ordinate showing the progressive degradation which is attendant on a rise of the ground water level, a decrease in acidity, a decrease in toxicity and, therefore, on an increase in the activity of microbiological agencies. According to White, the line A–A represents the condition under which vitrain was formed. In a

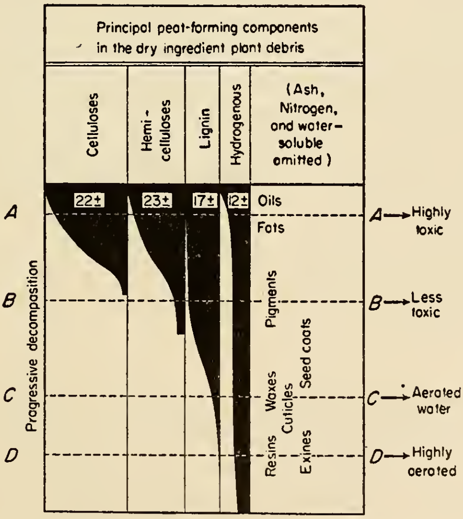

FIG. 5. White's coalification diagram.

similar way, the lines B–B, C–C, and D–D, refer to the genesis of clarain, durain and pseudo-cannel, respectively.

In the first stage (line A–A) practically all of the vegetable material is humified. Fragments with the lowest resistance (cellulose and hemicellulose) are hydrolyzed and partially decomposed, but their decomposition products participate in the humification process.

Next, the material is progressively decomposed (lines B–B, C–C); during stage C–C the much more resistant lignin is also broken down. Finally, only the most resistant fragments are preserved morphologically (line D–D).

In outward appearance, cannel coal shows a marked resemblance to pseudo-cannel, but contains less mineral matter and far more microspores. Genesis conditions of this coal must have been identical to those of pseudo-cannel; its parent material, however, had a quantitatively differing composition. Cannel coal is probably also produced in lakes and pools but, unlike pseudo-cannel, originates from floating spore accumulations transported by wind and water and deposited in the vegetable mud. An extreme variety of cannel coal is tasmanite, a light brown rock occurring in North Tasmania. Tasmanite is almost exclusively composed of spores, the dark ground mass being absent.

Outwardly, boghead is almost identical to cannel coal but it originates from a different parent material. Examined microscopically by transmitted light, boghead reveals a dark ground mass in which numerous white globules are embedded. The view that boghead is of algal origin is due to Bertrand and Renault (1892). Recent algal formations have also been discovered in the Balkash lake (Balkashite) and in Australia (Coorongite).

These algae, belonging to the group of Botryococcaceae, are very rich in proteins and fats and grow in rather deep and clear fresh water pools, that is to say in open lakes. It will be appreciated that in a Carboniferous swampy region these conditions were rather rare, thus explaining the sporadic occurrence of boghead coal. Potonié considered boghead coal to be a transition stage between true coal and mineral oil.

Progenitors

Chemical composition of plant tissues—We have seen that coal is a fossilized plant material and that every type of vegetable tissue has been converted into one or several macerals, the kind of maceral formed depending upon ecological conditions prevailing during genesis. The major plant fragments that have been preserved in coal originate from woody and cortical tissues on the one hand, and from the cork-like tissue of leaf cuticles and spore exines on the other. In addition, coal contains remains of resin duct fillings, etc.

The principal constituents of woody tissue are cellulose and lignin. Cellulose is a glucose-polymer and its structure is that of typically non-aromatic compounds. Lignin on the other hand is an aromatic substance. (see Chapter 3). It is the agent responsible for the lignification of vegetable tissue and, consequently, may be considered to be the cement that binds the cellulose fibers together into a firm structure.

The structural unit of cellulose, together with some probable structural units of lignin, have been compiled in Diagram 1.

Cork-like tissue of the type occurring in spore coats and cuticles is composed of fundamental units of typically aliphatic character such as fatty acids and wax alcohols on the one hand, and typically aromatic compounds such as lignin on the other.

Waxes, consisting of esters derived from fatty acids and wax alcohols, are non-aromatic in structure.

The principal constituents of resins are the resin acids with abietic acid as their best-known representative (Diagram 1).

Proteins, which are of essential importance in plant life because they constitute the fundamental units of protoplasm, only play a subordinate part in resistant plant tissue. The only trace that has been left of the proteins is nitrogen, which always occurs in low concentrations in the coal material.

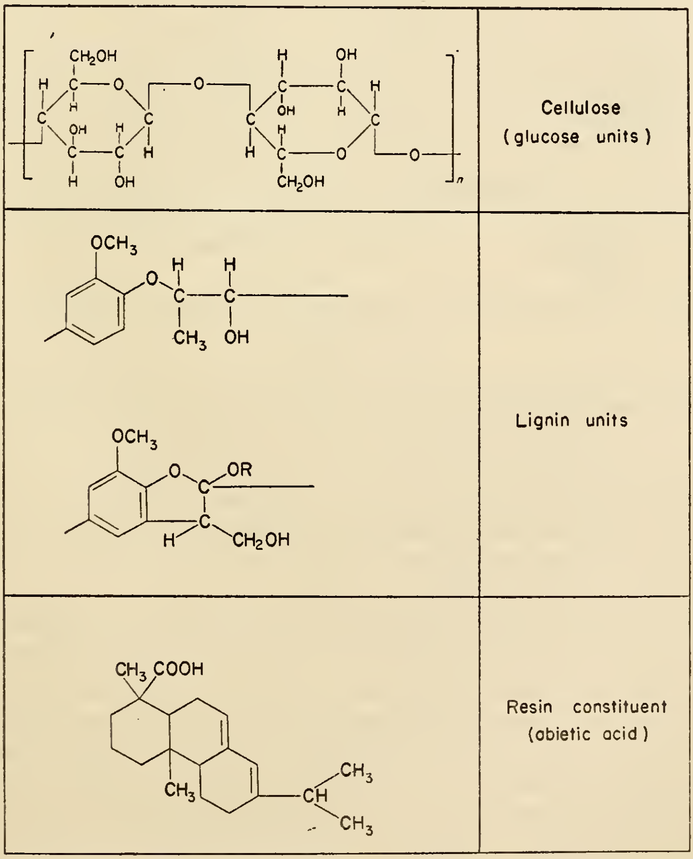

Diagram 1. Building units and constituents of principal plant chemicals.

Chemical coalification theories (Fischer and Schrader, 1922; Erasmus, 1938; van Krevelen and Schuyer, 1957)—It was originally believed that coal, and especially bright coal, was formed from cellulose because cellulose is the basic constituent of wood. This opinion was based on the results of artificial coalification experiments by Bergius (1913) who, starting with pure cellulose, succeeded in converting wood into a product showing some resemblance to natural coal. Maillard (1911, 1912, 1913) showed that sugars can be condensed into humic-like substances in the presence of amino acids. This furnished an indication of the mechanism by which cellulose might be converted into coal; i.e. hydrolytic decomposition into sugars followed by condensation with the degradation products of proteins.

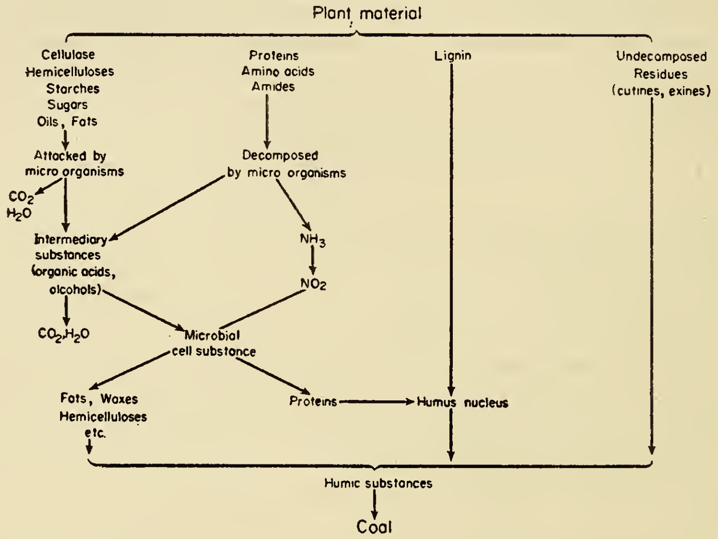

DIAGRAM 2. Schematic representation of formation of humus in the decomposition of plant residues according to A. S. Waksman.

In 1921 Fischer and Schrader advanced their theory in which they postulated that coal was not formed from cellulose but rather from lignin. According to these investigators, cellulose invariably undergoes bacterial decomposition. They showed, moreover, that swamps contain a high proportion of lignin. Their experiments proved that the cellulose content of plant debris decreases regularly in the course of the degradation process, but also that this decrease does not run parallel to the rise in humic acid content. In the case of lignin, however, this parallelism does exist and following initial increase, the concentration of lignin falls again owing to its gradual conversion into humic acids. Furthermore, humic acids were found to yield degradation products identical with those obtained from lignin.

At about the same time Eller and Koch (1920) and later Eller (1923) showed that oxidation of phenols generally leads to humic acid-like substances. Since lignin is also a phenolic compound, Eller's findings may be said to be in good agreement with the work done by Fischer.

The Fischer–Schrader theory has given rise to protracted and sharp controversies. Several investigators adhered to the cellulose theory and advanced extensive evidence in support of the correctness of their views. Others even went so far as to disclaim the presence of lignin in the plant body. They assumed that this substance is not produced until the wood is chemically treated, and ascribed its genesis to reactive carbohydrates or their decomposition products. The great microbiologist Waksman (1938) supported the lignin theory but established that proteins, in the form of autolysis products formed through the agency of bacteria, are essential for the synthesis of humic acids. Waksman's views are presented in Diagram 2.

A more recent theory compromising the above extremes, was advanced by Enders (1943) who, on the basis of Maillard's work, advanced the suggestion that humic acids formed from both cellulose and lignin. He visualized the formation of humic acids from carbohydrates in the following phases:

1. When natural conditions become unfavorable for the growth of micro-organisms, their metabolism changes. Although the normal decomposition of carbohydrates leads to carbon dioxide, the changed metabolism leads to the formation of methylglyoxal.
2. Under the influence of amino acids or protein decomposition products, methylglyoxal generally condenses very rapidly to form brown compounds that are still water-soluble; this reaction occurs at temperatures as low as 20°C.
3. As condensation advances, these soluble products are modified into true humic acids that are not soluble in water.

Enders succeeded in reproducing each of these stages in the laboratory. Because amino acids are important here, he believes that carbohydrate decomposition products play a part in the origin of the nitrogen-rich coals, whereas the nitrogen-poor varieties are mainly derived from lignin. A further explanation of Enders's views is given in Diagram 3. The chemistry of the conversion of methylglyoxal into humic acid probably proceeds via an aldol condensation with simultaneous cyclization.

Enders's theory seems to be of considerable importance, especially when viewed in the light of the recent work done by Flaig and Schulze (1952). These workers showed that the transformation of phenols (and, therefore, also of lignin) into humic acids may be divided into three stages: formation of oxyquinone, rupture of the rings to form very reactive keto acids, and subsequent reactions to yield condensed ring systems.

Carbohydrate decomposition products, i.e. reactive keto acids, show a fairly strong tendency toward aromatization. The ring structure of aromatic oxyquinones, on the other hand, may rupture easily, to form reactive keto acids, i.e. chain compounds. The controversy as to whether cellulose or lignin is to be considered as the parent material of coal becomes, therefore, more or less pointless if these considerations are correct.*

Inasmuch as the reaction mechanism of coalification must be exceedingly complicated from a chemical point of view, it must be expected that the final product, coal, will also possess a complicated, heterogeneous structure.

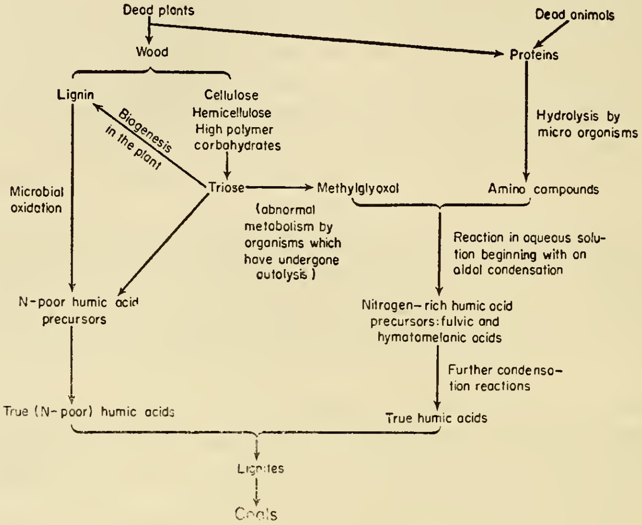
Dead plants
Dead animals
Wood
Proteins
Lignin
Cellulose
Hemicellulose
High polymer
carbohydrates
Biogenesis in the plant
Hydrolysis by micro organisms
Microbial oxidation
Triose
Methylglyoxal
Amino compounds
(abnormal metabolism by organisms which have undergone autolysis)
Reaction in aqueous solution beginning with an aldol condensation
N-poor humic acid precursors
Nitrogen-rich humic acid precursors: fulvic and hymatomelanic acids
Further condensation reactions
True (N-poor) humic acids
True humic acids
Lignites
Coals

Diagram 3. Mechanism of humification and coalification according to Enders.

Coalification Diagram—A very simple and rapid means for obtaining an insight into the course of the processes occurring during coalification is the "atomic H/C vs. O/C-diagram" introduced by van Krevelen (1950). The main constituents of coal are the elements carbon, hydrogen and oxygen. The elementary constitution of any term of the coalification series may be represented graphically by plotting its H/C-ratio versus its O/C-ratio. This method of graphical representation offers a number of advantages inasmuch as all simple reaction processes can be represented by straight lines. Figure 6 shows the lines describing the processes of dehydration, decarboxylation and demethanation.

The development lines of the various macerals can be plotted in the H/C vs. O/C-diagram. In this way the composition of vitrinites at any point of the development line (determined from microscopically homogeneous samples) is shown, and the band in which all of these values are located is called the "*vitrinization band*" (or coalification band). From the shape of this band it may be concluded that the primary coalification reaction is essentially a dehydration process which appears to be followed successively by decarboxylation and demethanation reactions.

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* Only in the extreme conditions that are responsible for the genesis of durain it is justifiable to say that cellulose has been fully degraded and that lignin together with exines have been the parent materials of coal.

The well-known humic acids that may be extracted from brown coal by alkaline solutions are always located to the right of the coalification bands of woody tissue (Fig. 7) and therefore seem to be composed mainly of oxidation products (Kreulen and Kreulen van Selins, 1956). The development lines of the other macerals are shown in Fig. 7. The pure maceral fusinite has a constant composition (H/C = 0.38; O/C = 0.01); the compositions of the various micrinites are located in a band parallel to the vitrinization band but with lower H/C-ratios.

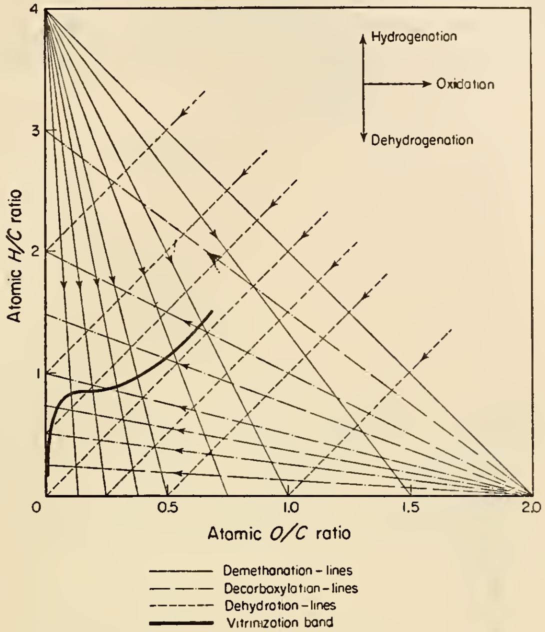


FIG. 6. H/C vs. O/C diagram.

An altogether different development line is that of the exinites. The chemical constitutions of cuticles, spore membranes, and corky tissue, which are all related to one another, are intermediate between those of plant waxes and lignins. This confirms the view that these plant constituents are combinations of wax alcohols and lignin units, just as wood is built up of complexes of cellulose and lignin.

The development lines of these macerals differ fundamentally from that of woody tissue, but in the vicinity of bituminous coal the differences in chemical constitution between vitrinite and exinite diminish steadily. Schopf (1948) termed this phenomenon "incorporation". Beyond this stage, it becomes increasingly more difficult to distinguish between these two macerals.

Resins and waxes are resistant to degradation in the first stage of coalification. Even in low rank bituminous coals, the resinous constituents have practically retained the composition of the parent resin. Therefore, these substances cannot be considered to have been coalified in the true sense of the word, although it must be admitted that they have undergone some polymerization and aromatization reactions.

Figure 7 shows that, in spite of all the differences cited, all development lines have one feature in common: increasing aromatization leading in the direction of pure carbon (graphite).

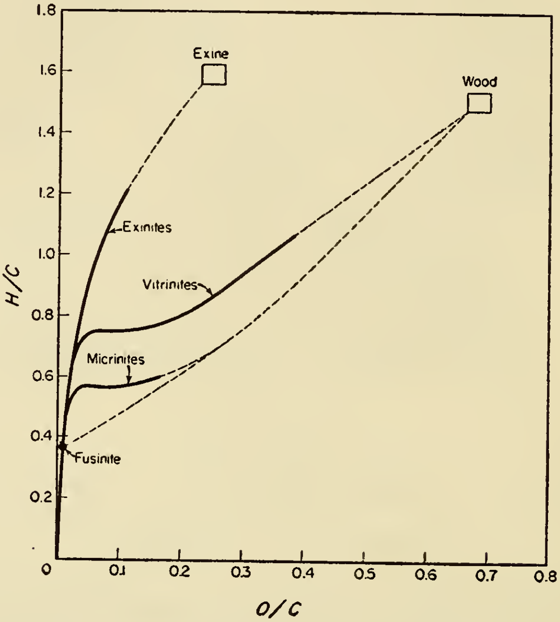


FIG. 7. Development lines of the macerals.

Physical and Chemical Properties of Coal

All properties of coal vary with elementary composition and hence with the degree of coalification or rank. The rank of coal is always expressed in terms of the carbon content of pure vitrinite which occurs, among other macerals, in the coal or coal seam.

Mention has already been made of the coalification diagram in which the variation in elementary composition of any maceral can be followed throughout the coalification range. For completeness, the hydrogen and oxygen contents of the macerals are plotted as functions of the carbon content in Figs. 8 and 9. Points of equal rank are connected by broken lines. At equal carbon content, micrinites are always poorer and exinites always richer in hydrogen than vitrinites; the reverse applies for oxygen. Differences between the macerals disappear progressively with increasing rank so that in coal of highest rank (anthracite) all macerals have become chemically identical.

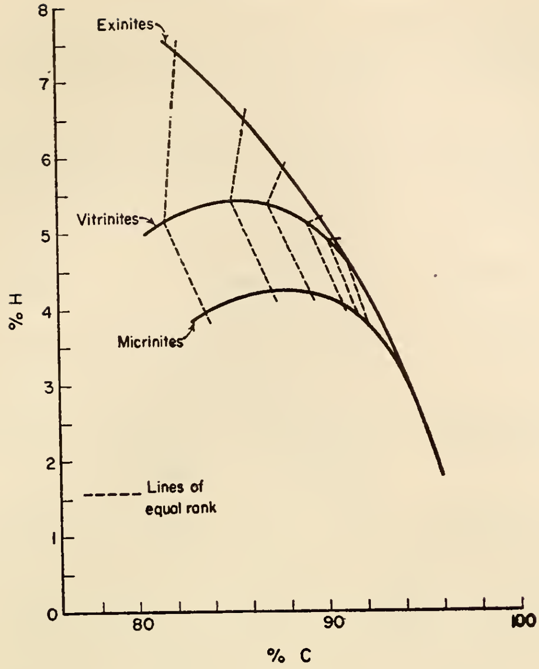


FIG. 8. Hydrogen content of coal macerals.

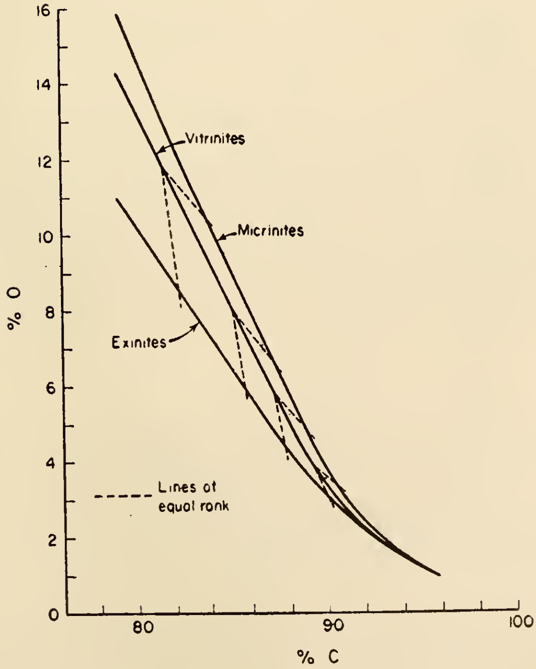


FIG. 9. Oxygen content of coal macerals.

The following properties of coal will be dealt with in succession:

Structural properties	(density, molar volume, porosity, texture)
Optical properties	(reflectance, refractive index, absorption index, spectral extinction)
Thermal properties	(expansion coefficient, specific heat)
Electrical properties	(dielectric constant, conductivity)
Magnetic properties	(diamagnetic susceptibility, paramagnetic resonance)
Mechanical properties	(sound velocity, elastic constants, hardness, grindability)
Sorptive properties	(solubility of gases, intrinsic moisture content, heat of wetting)
Chemical properties	(extractability, oxidizability, hydrogenatability)
Technological properties	(volatile matter, calorific value, agglutination, plasticity on heating, etc.).

Structural properties—The principal structural property of coal is its density, or its reciprocal value, its specific volume (Franklin, 1949; Dulhunty and Penrose, 1951). Densities of solids are measured with a pycnometer using a displacement medium. True density is measured with a medium (helium) capable of penetrating all the pores; the apparent density with a medium (mercury) which has practically no access to the pore system. The difference between the two values is the porosity or pore volume.

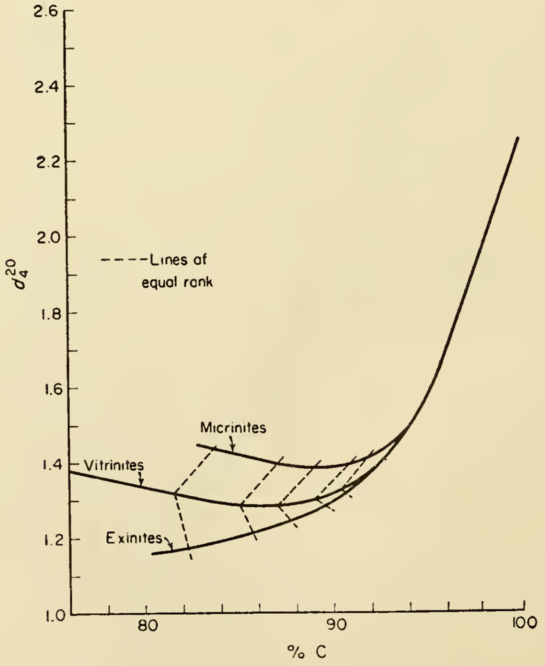


FIG. 10. Density of coal macerals.

From Fig. 10, where the densities of the various macerals have been plotted against carbon content, it can be seen that exinites have a lower, and micrinites a higher, density than vitrinites of the same rank; here, again, the differences gradually decrease with increasing rank. At higher ranks the density rapidly tends towards its limiting value (graphite).

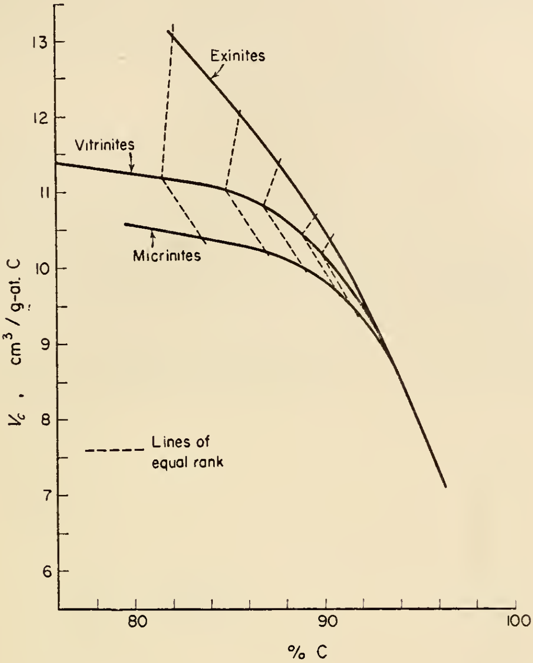


FIG. 11. Molecular volume (per C atom) of coal macerals.

An important function derived from the density is the molar volume, that is, the quantity M/d where M denotes the molecular weight.

The trouble is that the molecular weight of coal cannot be determined. What can be derived, however, is the molecular weight per carbon atom and, hence, the molar volume per carbon atom. This quantity, which can be calculated from

$$V_c = -\frac{1}{d}\,\frac{1200}{(\%\,C)}$$

is characteristic for the various macerals (see Fig. 11) and plays an important part in constitutional analysis.

Coal, being a colloidal solid substance, has a certain porosity and, consequently, an internal surface. Recent investigations (Malherbe, 1951; Malherbe and Carman, 1952; Maggs, 1952, 1953; Zwietering and van Krevelen, 1954; Zwietering, Overeem and van Krevelen, 1956; Bond, 1956) have shown that coal contains two pore systems: a system with a mean pore diameter of 500 Å and a pore size distribution ranging from 30 Å to 5μ, and a system of pores measuring 5 to 15 Å in diameter. The volume of the latter, the ultra-micropore system, is small (approximately 0.025 cm^3/g); its surface area, however, is very large (about 200 m^2/g). The former, coarser, pore system on the other hand has an internal surface area of no more than about 1 m^2/g. This system can be studied by measuring the degree of mercury penetration as a function of pressure, or by absorption tests at very low temperatures. Measurements on the ultramicropore system can be carried out by adsorption at normal temperature. These pores are so narrow that the rate of diffusion of gas molecules (with the exception of helium which can penetrate into it even at low temperatures) is strongly dependent on temperature (activated diffusion).

The atomic arrangement of a substance is reflected in its X-ray diffraction pattern. X-ray diffraction, therefore, is one of the major techniques for disclosing the ultrafine structure of coal. The diffraction patterns become more distinct with increasing rank and gradually come to resemble the pattern for graphite. This point will be discussed in more detail in the section dealing with structure.

Optical properties—The only optical property of coal that is relatively easy to measure is its power to reflect light. The percentage of incident light reflected by a polished surface is called *reflectance* (Hoffmann and Jenkner, 1933; Seyler, 1943, 1948, 1955; McCartney, 1952; Dahme and Mackowsky, 1950, 1951; Huntjens and van Krevelen, 1954; Broadbent

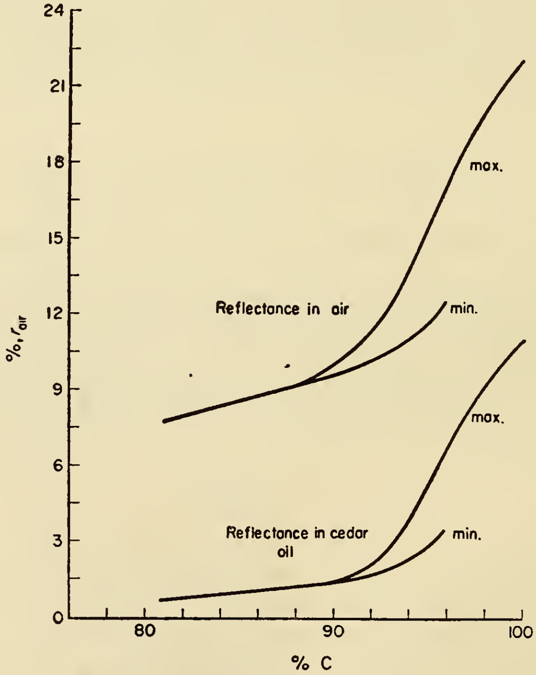


FIG. 12. Reflectance of vitrinites.

and Shaw, 1955). Berek (1931a, b) developed a method for measuring the reflectance on microscopic surfaces. In addition, the immersion technique provides a means for measuring the reflectance in various media (Stach, 1935, 1949).

The electromagnetic theory of light relates the reflectance of a solid to its *refractive* and *absorption indices.* By measuring these indices in two media, two new optical properties can be derived using the relationship:

$$r = \frac{(n - n_0)^2 + (nk)^2}{(n + n_0)^2 + (nk)^2}$$

where r = reflectance
n = refractive index of the sample
k = absorption index of the sample
n_0 = refractive index of the medium.

The values of the optical quantities of the coal macerals can be read from Figs. 12–15. Vitrinites beyond the rank corresponding with 85% carbon are anisotropic and consequently have two refractive indices, one perpendicular and one parallel to the bedding plane. Micrinites and exinites are isotropic, the former having a higher, the latter a lower refractive index than vitrinite.

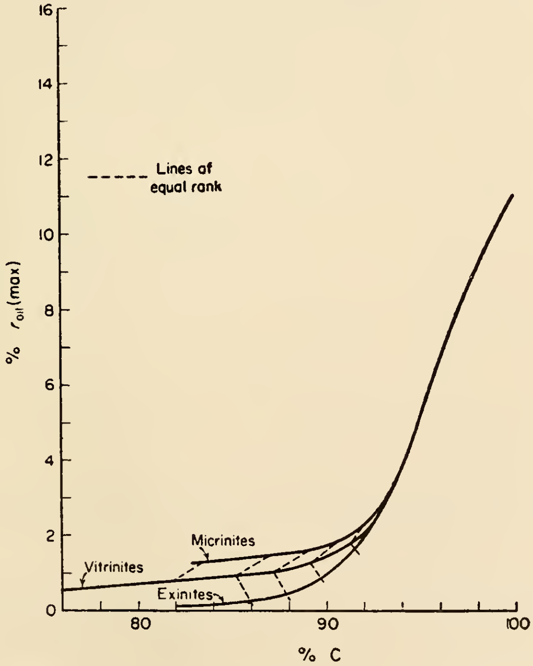


FIG. 13. Reflectance (in cedar oil) of coal macerals.

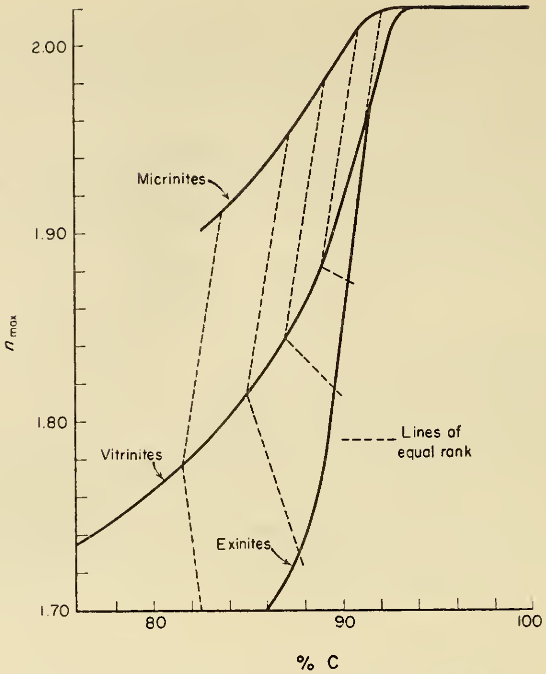


FIG. 14. Refractive index of coal macerals.

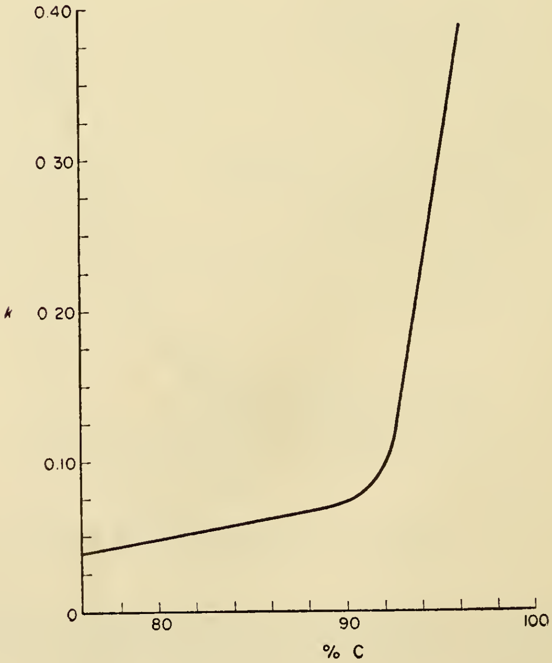


FIG. 15. Absorption index of vitrinites.

An important function derived from the refractive index is the molecular refraction:

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

Since the molecular weight of coal cannot be measured, we have to satisfy ourselves again with determining the *molar refraction per carbon atom*:

$$r_c = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \cdot \frac{1200}{(\% \text{ C})}$$

This function also plays an important part in the constitutional analysis of coal (Fig. 16).

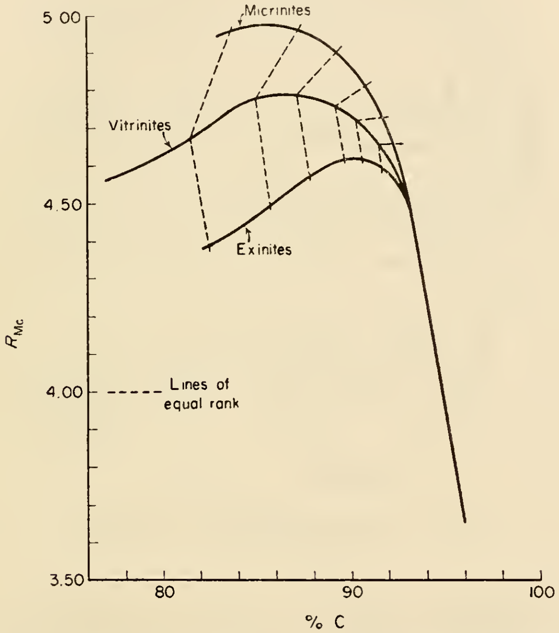


FIG. 16. Molecular refraction of coal macerals (per C atom).

Besides the classical optical constants, the *absorption spectrum* of coal must also be mentioned. The spectrum in the visible region and the ultraviolet is completely continuous and the extinction coefficient increases with rank.

The infrared spectrum, on the other hand, shows characteristic absorption bands (Fig. 17) which point to the occurrence of O—H, C—H_{al}, C—H_{ar}, $>$C=O, C—O—, (—C=C—C=C—$)_{ar}$ and other frequencies. Here again, background absorption strongly increases with rank. The infrared spectrum provides valuable information on coal constitution and confirms many conclusions obtained by other (chemical) methods (Cannon *et al.*, 1944, 1945, 1953; Gordon, Adams, and Jenkins, 1952; Gordon *et al.*, 1954; Brown, 1955; Bergmann *et al.*, 1954; van Vucht *et al.*, 1955).

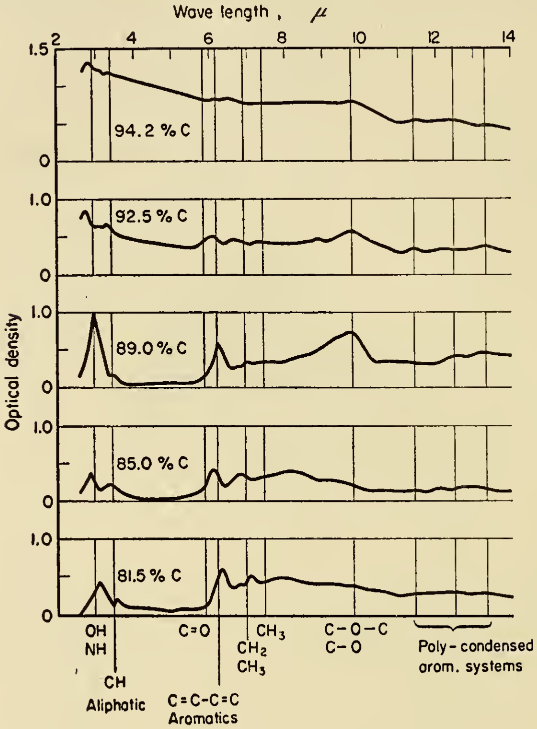


FIG. 17. Infrared spectra of vitrinites.

Thermal properties—The only thermal properties that have been accurately examined so far are the *expansion coefficient* (Schuyer and van Krevelen, 1955; Joy, 1955) and the *specific heat* (Clendenin, 1949). The mean expansion coefficient is maximum at 85% carbon. At this rank thermal "anisotropy" becomes noticeable (Fig. 18). Specific heat as a function of rank is plotted in Fig. 19. After a gradual decrease with increasing rank the curve shows a break at about 91% carbon.

Electrical Properties—Among the electrical properties the *dielectric constant* (ϵ) (Groenewege *et al.*, 1955) and the *electrical conductivity* (Schuyer and van Krevelen, 1955) are the most important. According to Maxwell's theory the dielectric constant of insulators having no permanent dipole moment is equal to the square of the refractive index.

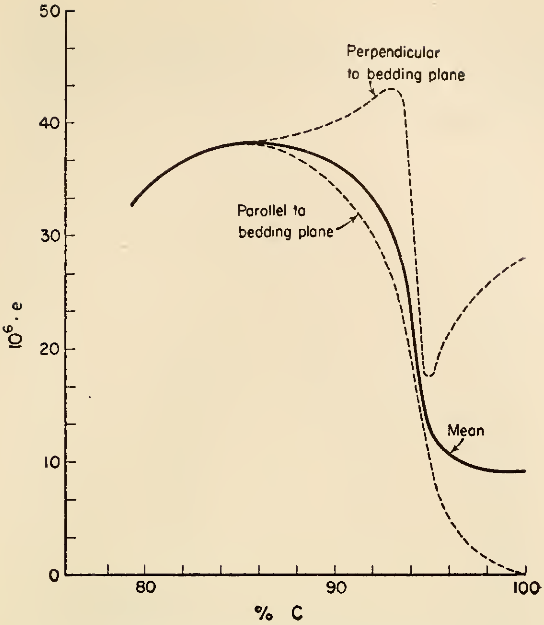


FIG. 18. Thermal expansion coefficient (vitrain).

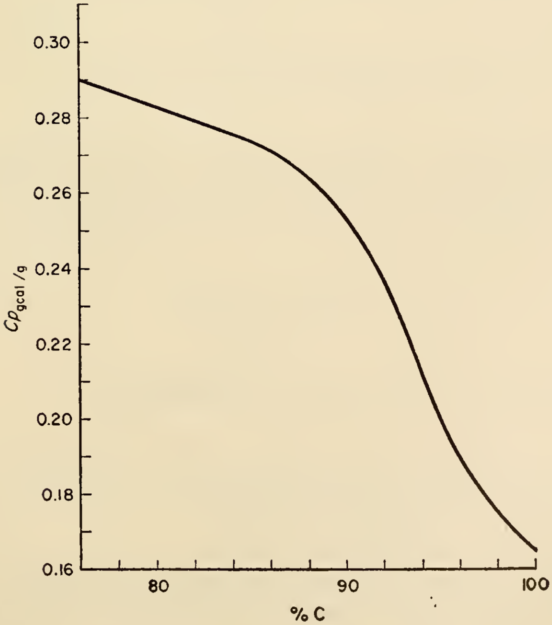


FIG. 19. Specific heat (vitrain).

In the case of coal (Fig. 20) this only holds true at carbon contents of about 87 per cent. At lower and higher carbon percentages $\epsilon > n^2$; in the former case this must be attributed to the effect of permanent dipoles, in the latter to semi-conductance.

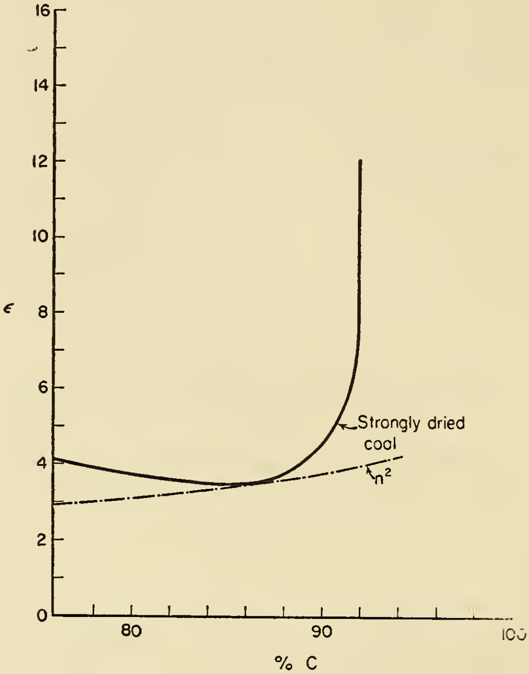


FIG. 20. Dielectric constants (vitrains).

The specific electrical resistance falls off rapidly at carbon contents above 87%; at high rank its value decreases exponentially with rising temperature according to the well-known relation for semi-conduction:

$$\rho = A \exp\left(\frac{\Delta U}{2kT}\right)$$

The energy barrier ΔU is a function of rank (Fig. 21).

Magnetic properties—Investigations into the magnetic properties of coal are very recent. The most important of these are the *diamagnetic susceptibility* and the *paramagnetic resonance.*

The diamagnetic susceptibility (Honda and Ouchi, 1957) strongly depends on the aromatic character of the material. Its value increases with rank, especially beyond 91% carbon, when a sharp rise is observed (Fig. 22). Paramagnetic resonance is a measure of the concentration of free radicals

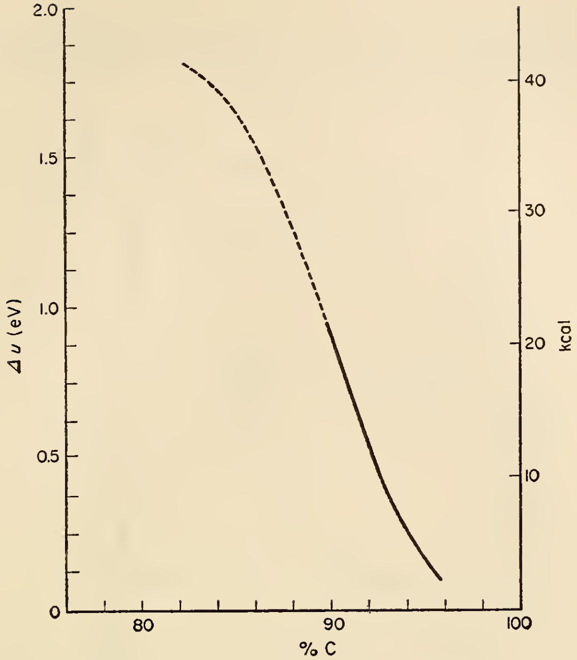


FIG. 21. Energy barrier of electrical conductivity (vitrains).

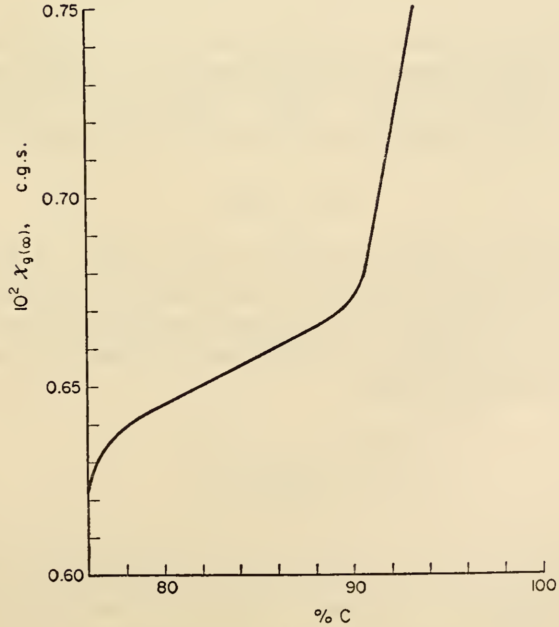


FIG. 22. Diamagnetic susceptibility (vitrains).

in coal (Ingram *et al.*, 1954; Uebersfeld, 1954; Uebersfeld *et al.*, 1954). The concentration of the free radicals is of the order of 10^{19} radicals per gram, that is, 1 per 2500 carbon atoms (Fig. 23).

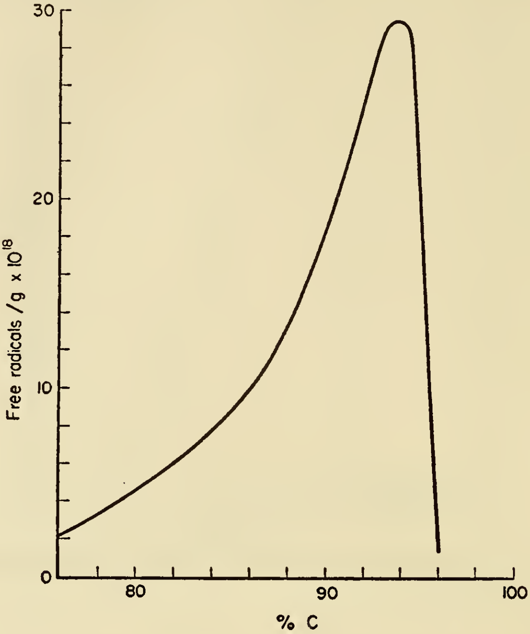


FIG. 23. Paramagnetic resonance (vitrains).

Mechanical properties—The elastic properties of coal can be derived from sound velocity measurements (Schuyer *et al.*, 1954, 1955; Inoue, 1951, 1953; Inoue and Tani, 1953). Although full consideration of formulas by which calculations are made cannot be given, they all have the shape:

$$dv^2 = f(a)$$

where d is density, v velocity of sound and a an elastic constant.

Curves for the elastic properties of the vitrains, i.e. sound velocity (v), Young and shear moduli (E and G), Poisson modulus (μ) and compressibility (K), are shown in Figs. 24–27. The relations between these quantities (for isotropic substances) are:

$$\begin{aligned} EK &= 3(1 - 2\mu) \text{ and} \\ E &= 2G(1 + \mu) \end{aligned}$$

At carbon contents of 91% and above the elasticity becomes anisotropic.

Other mechanical properties, depending among others on texture and plasticity, are *grindability* (Dryden, 1951b) and *hardness* (Inoue, 1953; van Krevelen, 1953) (Figs. 28 and 29). At 90% carbon these quantities

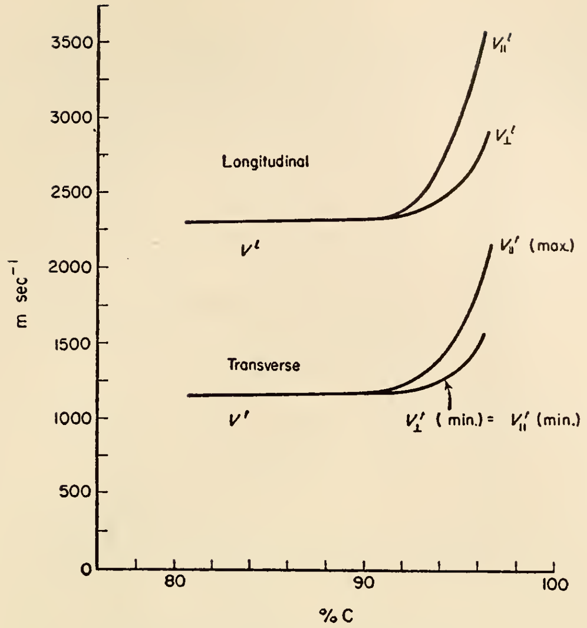


Fig. 24. Sound velocity (vitrains).

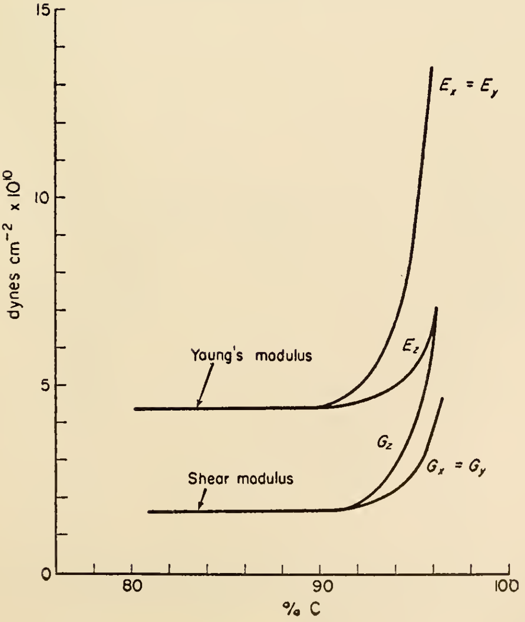


Fig. 25. Elastic constants (vitrains).

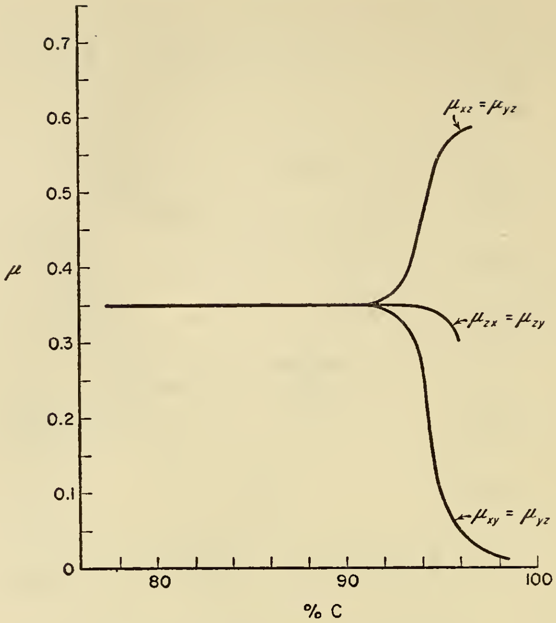


FIG. 26. Poisson's ratio (vitrains).

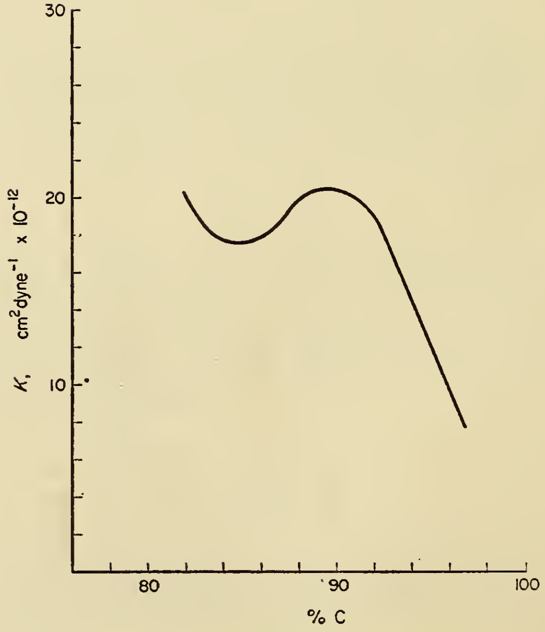


FIG. 27. Compressibility (vitrains).

also show a characteristic point, namely, maximum grindability and minimum hardness. The results of microhardness tests suggest that in the range of rank beyond 92% carbon coal becomes completely elastic. At very high pressures practically all coals show plastic deformation.

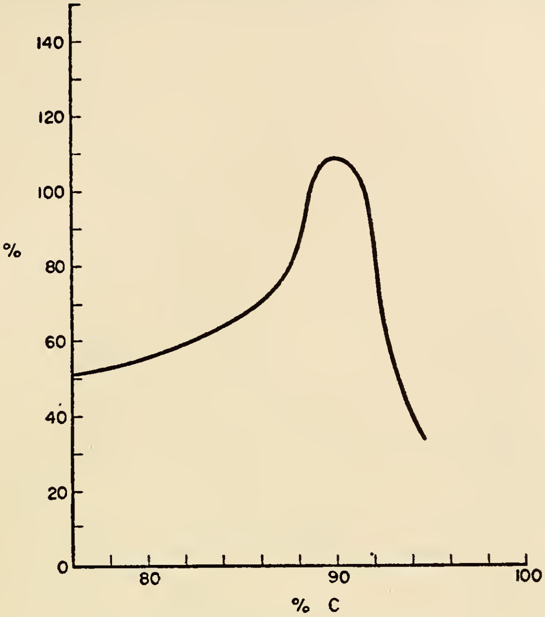


FIG. 28. Grindability (vitrains).

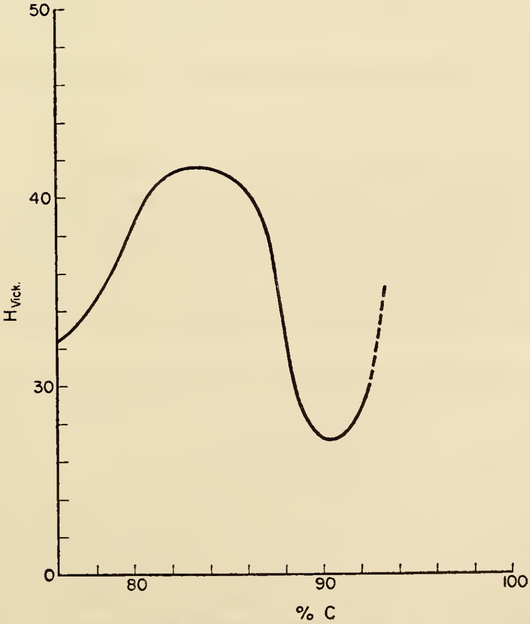


FIG. 29. Vicker's microhardness (vitrains).

Sorptive properties—Coal owes its sorptive capacity to its internal surface and partly also to the polar functional groups it contains. Practically all gases can be dissolved in coal to a greater or lesser extent. Of particular importance is the *sorption of methane* in connection with its occurrence in the coal seams (Fig. 30) (Chodot, 1952; van der Somme *et al.*, 1955).

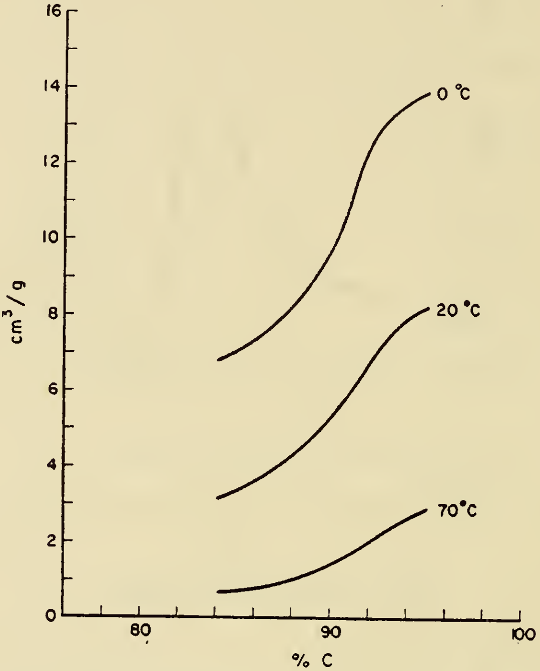


FIG. 30. Sorption capacity of coal for methane (vitrains).

A point of both scientific and practical importance is the *intrinsic moisture* content (Fig. 31); aside from low rank coals, this is highest in coal of both high porosity and high carbon content (Dulhunty, 1948).

Finally, the *heat of wetting* in polar liquids (methanol) should be mentioned; this quantity also depends on the combined effect of internal surface and polar groups (Fig. 32) (Griffith and Hirst, 1944).

Chemical Properties—Among the chemical properties, in a more restricted sense, we may count the behavior of coal during *solvolysis* (*extraction*), *oxidation*, and *hydrogenation*. In a certain sense the technological properties also come under this group.

Well-known extraction agents are pyridine (Wynne-Jones *et al.*, 1952) and ethylenediamine (Dryden, 1950a, b, 1951a, b, 1952). These solvents cause the coal to swell, after which the components of the lowest molecular weight pass into solution partly as molecules and partly as colloidal particles. It has not been established as yet whether we are

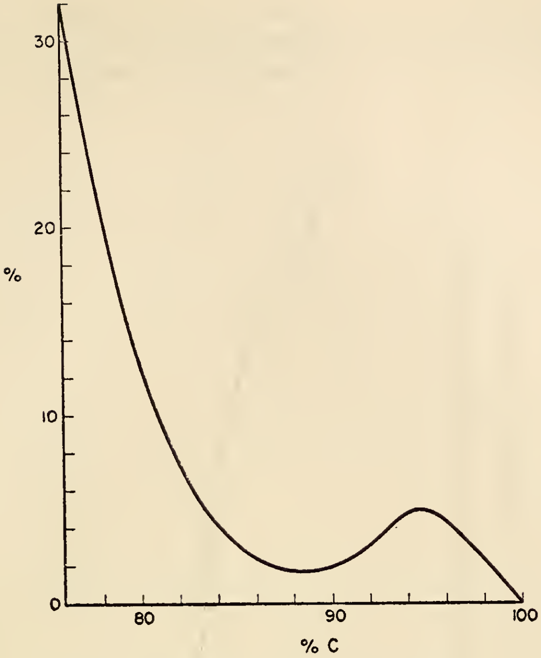


FIG. 31. Intrinsic humidity (vitrains).

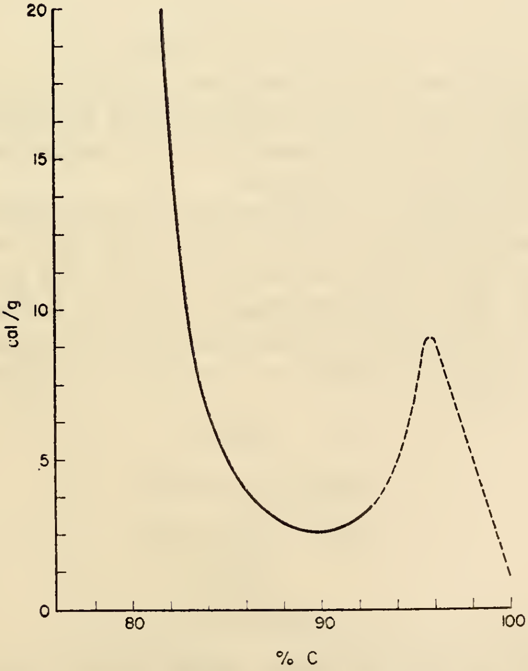


FIG. 32. Heat of wetting (vitrains).

concerned here with a purely physical or with a chemical effect. In Fig. 33 the extraction yields have been plotted versus rank. It can be seen from the figure that at 90% carbon the extractability of coal stops altogether.

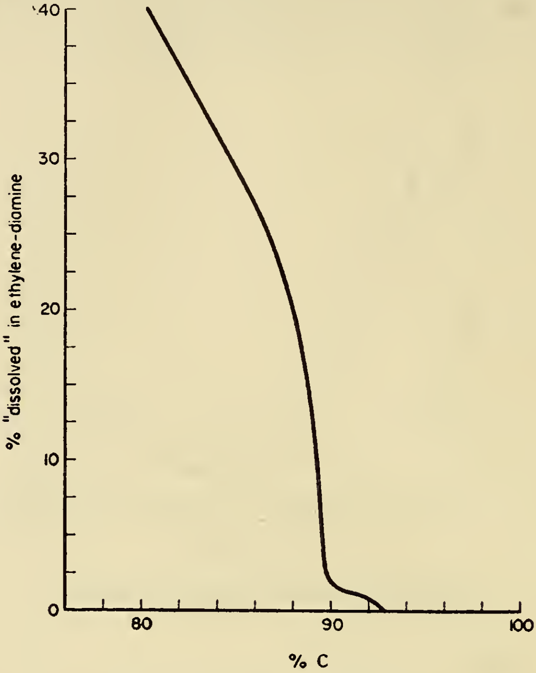
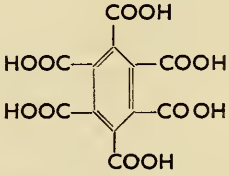


FIG. 33. Solvolysis (vitrains).

The behavior of coal during hydrogenation (Fisher *et al.*, 1940a, b) is also characteristic. Up to 88% carbon the yield of liquid products increases gradually; beyond this point the yield decreases very rapidly to approach zero at 91% carbon (Fig. 34).

Oxidation with agents such as nitric acid (Juettner, 1937a, b; Juettner *et al.*, 1937) and permanganate (Bone *et al.*, 1926, 1930, 1937) yields not only carbon dioxide, acetic acid, and oxalic acid, but also a variety of aromatic acids. The most characteristic of these is mellitic acid. From Fig. 35 it can be seen how the yields of mellitic acid increases with rank. Owing to its structure, mellitic acid furnishes an indication of ring condensation in coal.



mellitic acid

The reactivity of coal with gaseous oxygen (Kreulen *et al.*, 1938) can be determined from the rate at which the so-called "regenerated acids"

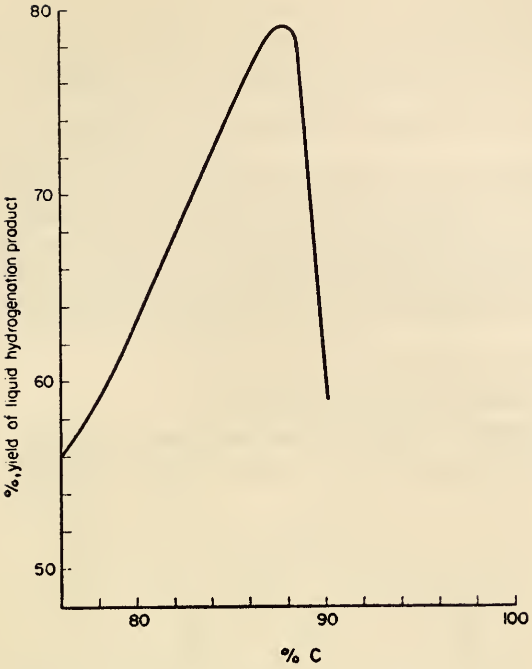


FIG. 34. Hydrogenation (vitrains).

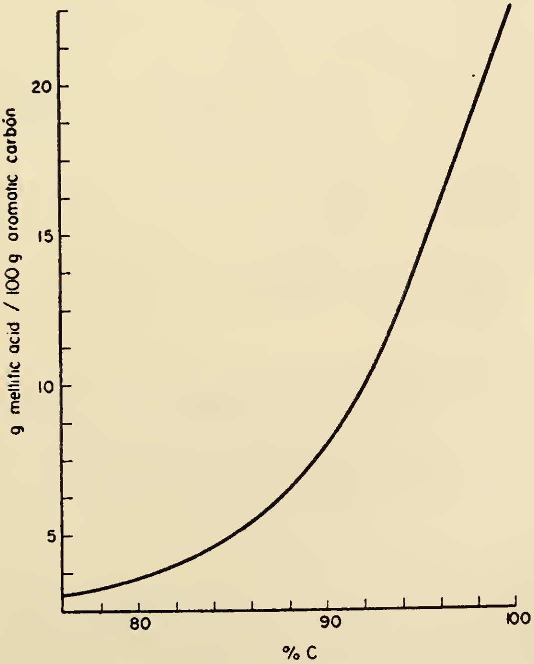


FIG. 35. Oxidation in acidic medium (vitrains).

are produced. In Fig. 36 the measured gross activation energies of this reaction have been plotted versus rank. The lower the activation energy, the higher the oxidation rate, according to the formula

$$r \text{ (rate)} = \text{const. } \exp(-E/RT)$$

Technological properties*—The technological properties provide an insight into the suitability of coal in the various fields of applications, especially in combustion and the production of coke and gas. For example, whereas softening and strong caking are nuisances in grate-firing practice, it is exactly this property that determines the suitability of coal for coke production.

The principal technological properties are:

1. *calorific value* (heat of combustion),
2. *volatile matter content* (precentage loss in weight on very rapid heating to 900°C, a quantitative measure of the evolution of gas and tar),

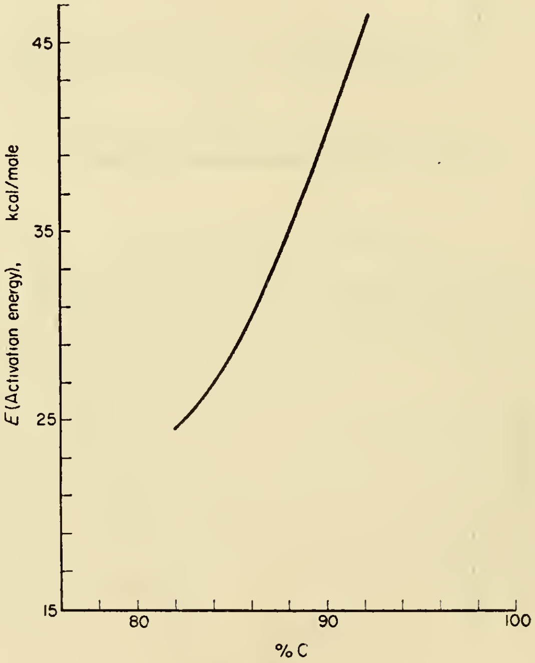


Fig. 36. Oxidation with air (vitrains).

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* See Methods of Analysis of Coal and Coke, *Fuel Res. Bull.* No. 44, London; A.S.T.M. Standards on Coal and Coke, Phila.; Audibert, 1926; Audibert and Delmas, 1927; Arnu, 1934a, b; Boyer, 1952; Dryden and Griffith, 1954; Giesler, 1934; Gray, 1923; Macura, 1938, 1939, 1940a, b, 1941, 1943a, b, 1944a, b, c, d; Roga, 1949.

3. *swelling* on rapid and slow heating (swelling index* and dilatometer index*)
4. *agglutinating power*, with respect to inert substances, on rapid and slow heating (Roga index* and Gray–King index*)
5. *characteristic temperatures* (softening, maximum fluidity, maximum gas evolution, and resolidification),
6. *degree of fluidity* of coal in the plastic state.

A graphic representation of these properties is shown in Figs. 37–44. The calorific value is highest in exinites and lowest in micrinites. Exinites have the highest volatile matter content, micrinites the lowest. Here again, vitrinites hold an intermediate position.

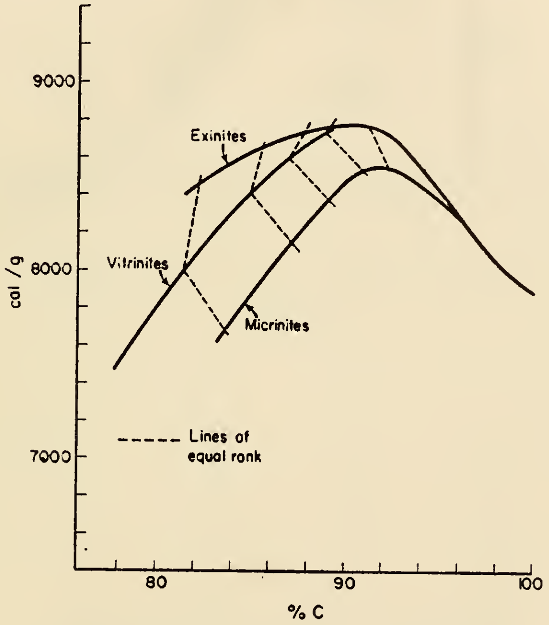

FIG. 37. Heat of combustion of coal macerals.

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* These practical parameters have the following significance: The free-swelling index is indicated by a figure corresponding with the profile of a coke button obtained under standard conditions; the dilatometer index denotes the maximum percentage elongation of a coal artifact (pencil) during slow heating under standard conditions; the Roga index gives the result of an abrasion test carried out with a coke button in a drum rotating a standardized number of revolutions, the resistance to abrasion being expressed as a percentage; the Gray–King index (*A*–*G*) describes the appearance of the coke button on slow heating. The letter *G* denotes that the coke button is smooth and just not swollen. If the coal is strongly caking and swelling, the coal is blended with electrode carbon. The subscript to the *G* gives the number of parts of electrode carbon added per 20 g of the mixture in order to obtain type *G*.

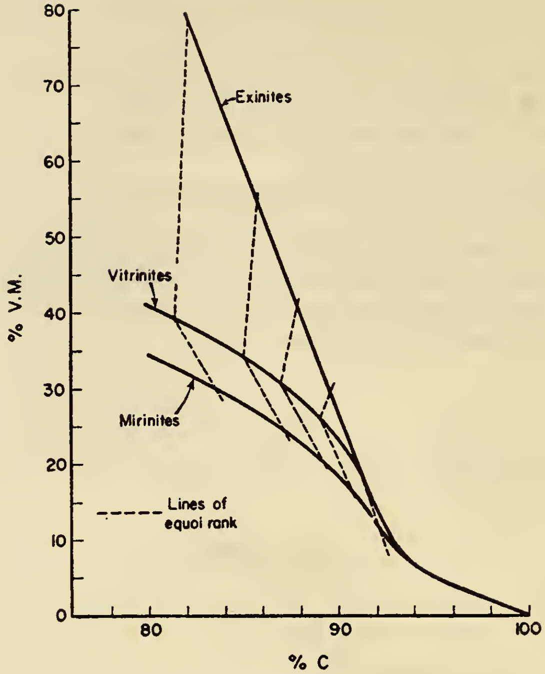

FIG. 38. Volatile matter of coal macerals.

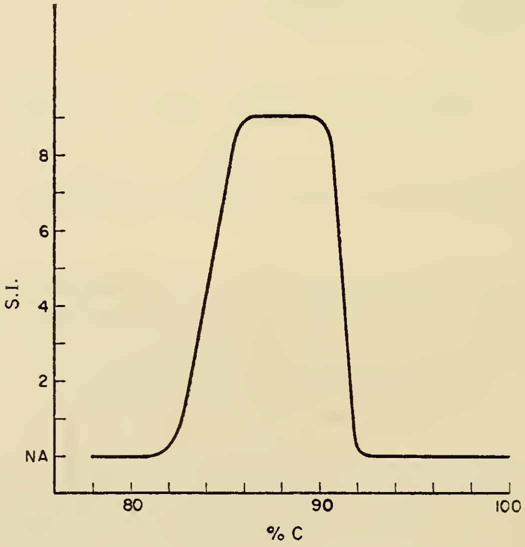

FIG. 39. Free swelling index of vitrains (average values).

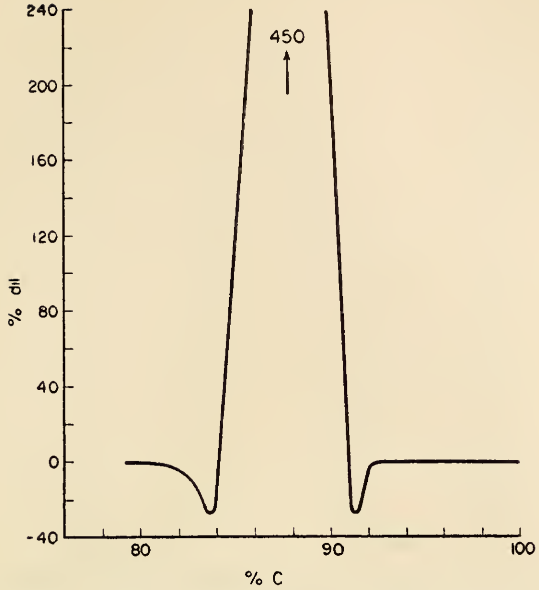

FIG. 40. Dilatometer index of vitrinites (average values of maximum dilation).

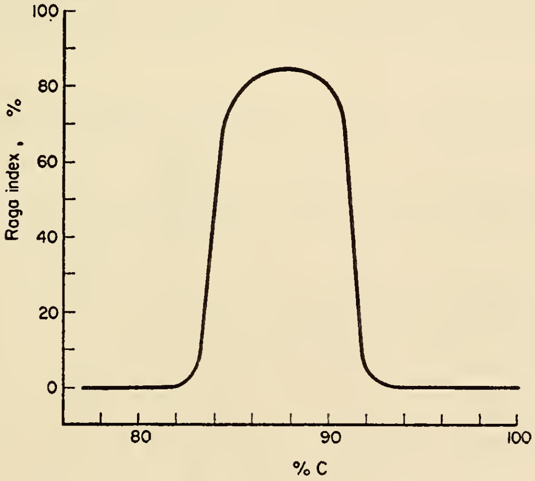

FIG. 41. Roga index of vitrains (average values).

Swelling on heating is greatest for the exinites; this maceral leaves very little solid residue. Vitrinites show the greatest coking power. Micrinites neither soften nor swell. Analogous conclusions hold for the agglutinating power.

The characteristic temperature diagram clearly shows the coalification range in which the vitrinites become plastic on heating. Coals of this range of rank possesses a certain degree of fluidity (normally determined with the Gieseler plastometer).

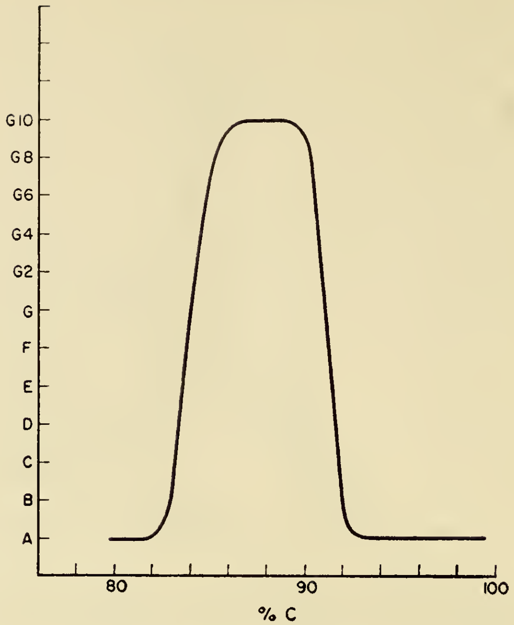

FIG. 42. Gray–King index of vitrains (average values).

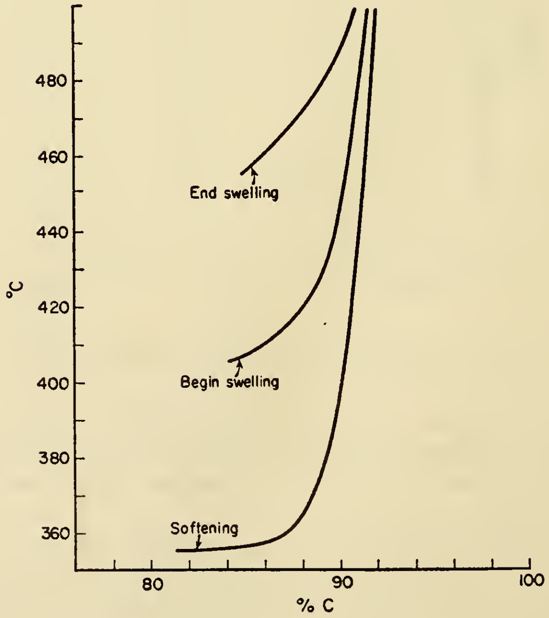

FIG. 43. Characteristic temperatures of vitrains (average values in dilatometer test).

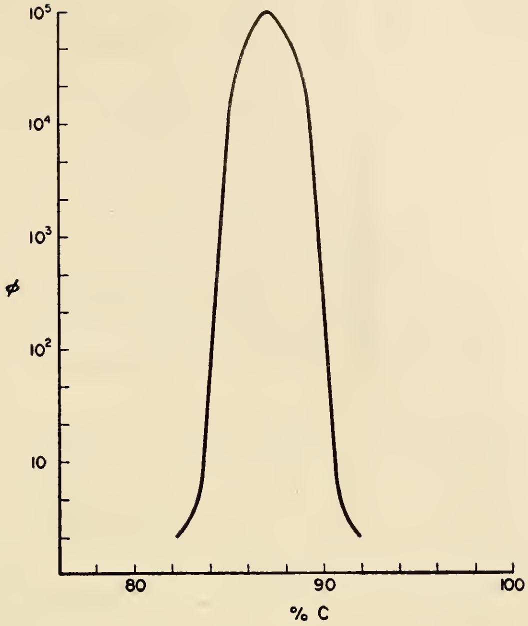

FIG. 44. Gieseler plasticity of vitrains (average maximum values).

Structure and Constitution of Coal (see also van Krevelen and Schuyer, 1957).

Study of the properties of coal has led to the development of a general structural picture, or rather two complementary structural pictures, one physical and one chemical.

X-ray analysis has been most important among the methods for arriving at the physical structural picture. As already pointed out, the X-ray diffraction pattern of coal resembles a very blurred graphite pattern similar to that obtained with activated carbons and carbon black (Fig. 45).

Starting with Warren's work on the structure of amorphous carbon, Blayden, Gibson and Riley (1944) introduced the concept of the turbostratic lamellar structure of coal. Riley visualized the coal molecules as flat, polynuclear aromatic molecules whose dimensions and degree of ordering increase with rank. A stack of ordered lamellae forms a crystallite. Assuming, furthermore, that the size of the lamellae shows a broad distribution curve, this simple picture permits explanation of several widely differing properties of coal. In the first place, it permits an interpretation of the X-ray pattern; furthermore, it provides a working hypothesis for explaining the phenomena observed during extraction and softening on heating. According to this picture the smallest lamellae are extractable and become mobile on heating, thus implying that they will act as a "lubricating agent" in the softening process.

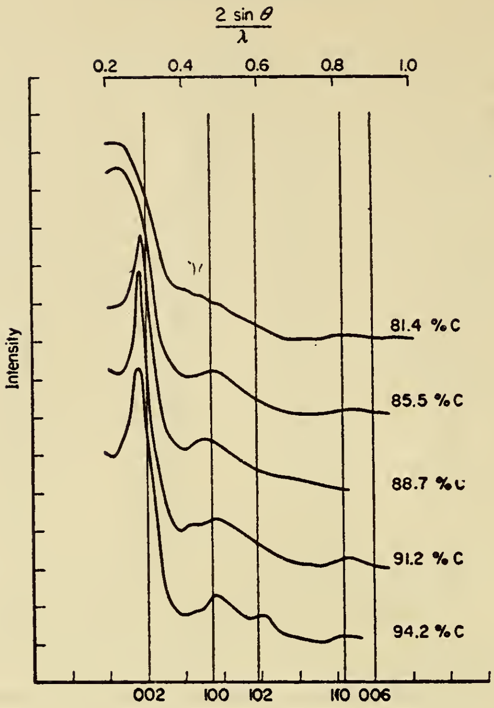

FIG. 45. X-ray diffraction curves of vitrains.

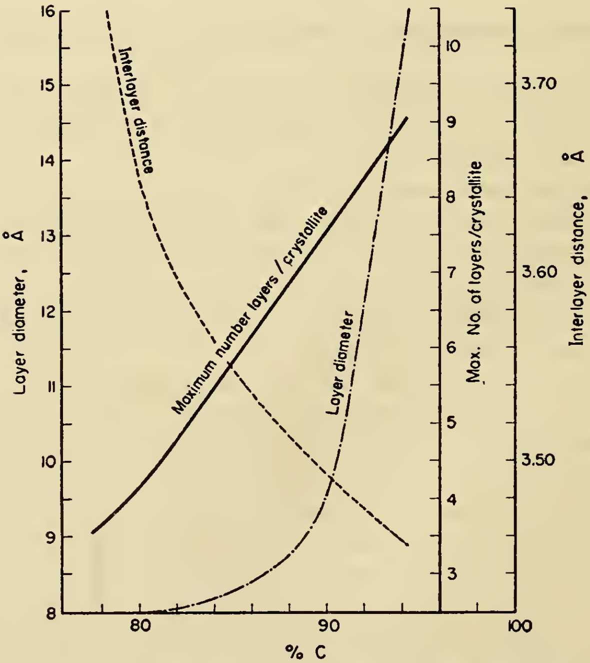

FIG. 46. Crystallite dimensions according to Hirsch.

In a quantitative respect, Riley's structural picture has been perfected by Hirsch (Hirsch, 1954; Brown and Hirsch, 1955; Cartz, Diamond and Hirsch, 1956), whose X-ray technique and calculation methods were much more accurate than those used by Riley.* From patterns recorded at high, low, and very low scattering angles, Hirsch derived information on the dimensions of the "coal molecules", the packing of the molecules, and the pore size distribution, respectively. Hirsch derived crystallite dimensions smaller by a factor of two than those reported by Riley, and showed that the degree of ordering increases with rank. Although the majority of the crystallites in coal consist of stacks of 2–3 lamellae, the maximum number of lamellae per stack increases from 4–5 at 80% carbon to 8–10 at 94%. The interlayer distance meanwhile decreases from about 3.65 to 3.43 Å. Figure 46 shows the variation in layer diameter and inter layer distance found by Hirsch.

On the basis of his investigations, Hirsch distinguished three structural stages in the coalification process. Below 85% carbon, coal shows a so-called "open structure": the lamellae are almost randomly orientated and are connected by cross-links. Between 85 and 91% carbon, coal possesses a "liquid structure". Many cross-links are ruptured and there is some degree of orientation. Beyond 91% carbon, coal shows an anthracitic structure; not only the lamellae but also the pore system becomes highly oriented (Fig. 47).

The chemical structural picture has resulted partly from a study of the relationship between chemical constitution and physical properties and partly from purely chemical investigations dealing mainly with the determination of functional groups.

Van Krevelen *et al.*, by studying the true density and optical properties of coal, gathered information on three very important constitutional parameters: aromaticity (f_a, i.e. the fraction of carbon atoms present in aromatic structures), ring condensation index (i_R, i.e. the fraction of carbon atoms at the junctions of the ring structures), and the mean dimensions of the aromatic clusters (C_a, i.e. the number of aromatic atoms belonging to one condensed ring system).

It is well known that the molar volume* ($V_m = M/d$) of vitreous substances and liquids may in principle be composed of contributions from the atoms each of which has its own characteristic atomic volume. The molar volume of aromatic and cyclic compounds, however, is smaller than would follow from the atomic contributions. As a result, studies of the density permit conclusions to be drawn about aromaticity and ring condensation index.

Information about the dimensions of condensed aromatic systems may be derived in an analogous way from optical data (refractive index). The molar refraction* of saturated substances can be calculated from the atomic contributions. For aromatic substances, however, the additivity principle does not hold, and these compounds show enhanced molar refraction. This explains why the refractive index, in combination with density and elementary composition, provides information on the size of the aromatic clusters.

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* In a more recent publication Hirsch (1958) communicated slightly altered values.

* Actually the molar volume or molar refraction *per carbon atom* is the most appropriate in coal research.

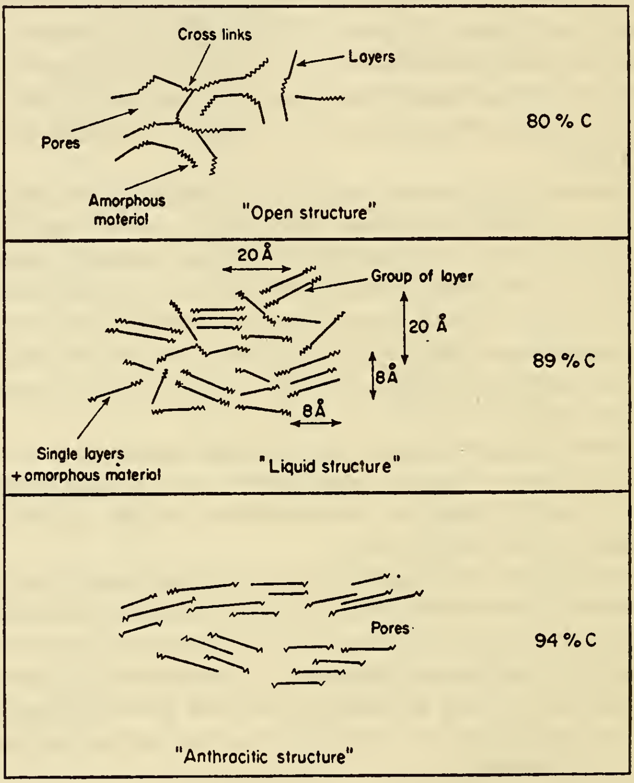

FIG. 47. Structural model of coal, according to Hirsch.

The results of these studies have been compiled in Figs. 48–50, from which it can be seen that the aromaticity of all macerals (except fusinite) increases sharply with rank; micrinites are rather strongly aromatic, whereas exinites of low rank have a low aromatic content; vitrinites hold a middle position. The macerals differ considerably with regard to the degree of ring condensation. At the start of the coalification process, exinites are weakly condensed and micrinites are fairly strongly condensed; vitrinites again take a middle position. At about 91% carbon, the ring condensation index starts rising sharply with rank; this also holds for the mean size of the aromatic clusters. At first the clusters in exinite are very small with an average of only one benzene ring. In vitrinites of this range of rank they are also small; at the transition from lignite to coal only 2–4 rings per cluster. At higher rank the size of the clusters increases rapidly.

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* Actually the molar volume or molar refraction *per carbon atom* is the most appropriate in coal research.

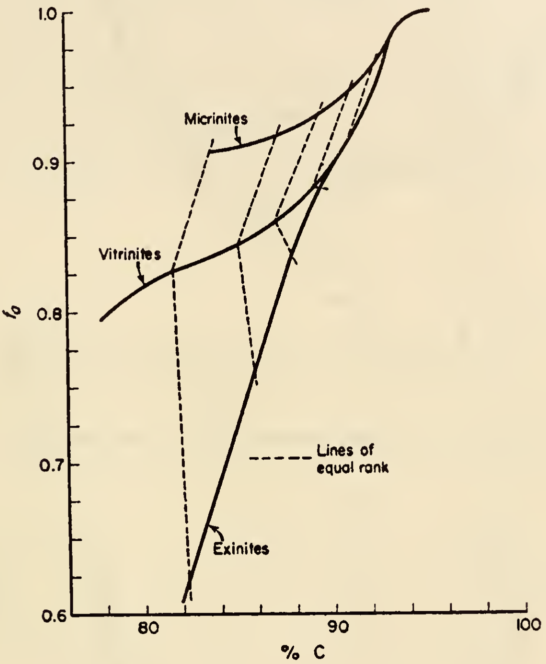


FIG. 48. Aromaticity of coal macerals.

This chemical picture of the carbon skeleton is confirmed by data obtained by other methods of investigation. For example, the ratio between the intensities of the infrared absorption bands of aromatic and aliphatic CH-groups provides a clear indication of the strong relative decrease in the number of aliphatic groups with increasing rank. At 93% carbon, coal has become completely aromatic (see Fig. 51) (Brown and Hirsch, 1955).

Besides this structural analysis of the carbon skeleton, functional group analysis also permits an insight to be gained into the peripheral, mainly oxygen, functions (Ihnatowice, 1952; Blom *et al.*, 1957) (Fig. 52). During the transition from lignite to high volatile bituminous coals, the methoxyl groups disappear first and then the carboxyl groups, while the content of carbonyl groups also decreases considerably. In the range of 81 to 89% carbon, the content of OH-groups falls off rapidly.

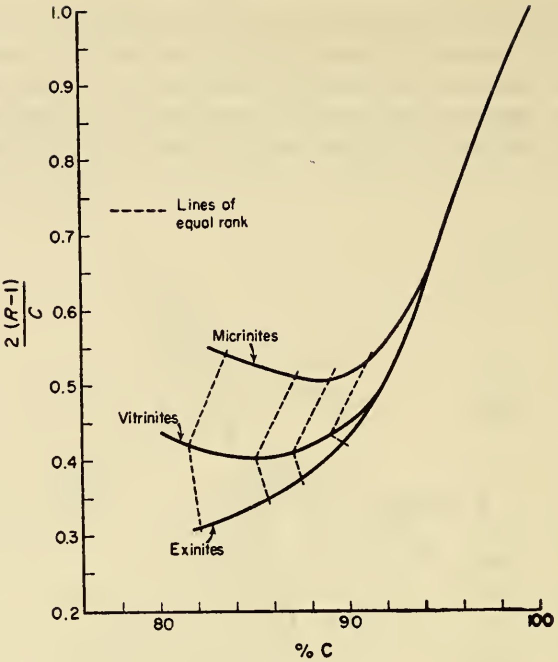


FIG. 49. Ring condensation index of coal macerals.

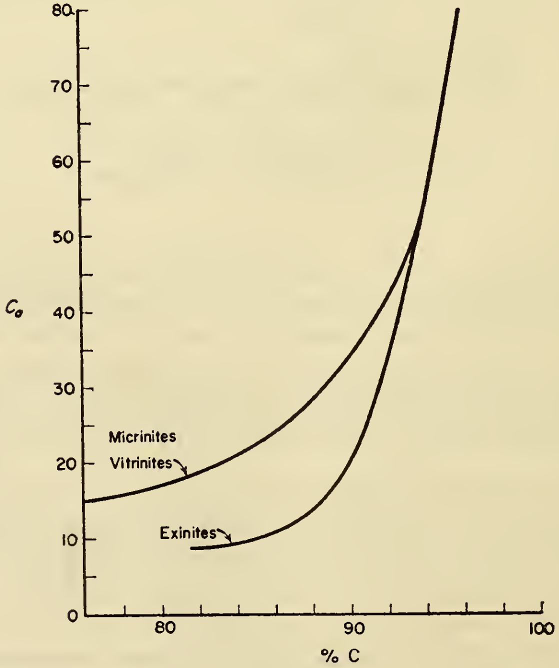


FIG. 50. Number of aromatic C atoms per structural unit.

Beyond 92% carbon practically all oxygen is present in non-reactive, exceedingly stable, configurations.

The nitrogen in hard coal probably occurs almost completely in cyclic structures.

The structural picture of the coal matrix (vitrinite), as we know it today, may be briefly summarized as follows: Coal possesses a composition similar in some respects to that of substances like pitch and bitumen, being made up of a large number of chemical units that are identical in type but very different in molecular fine structure and molecular weight. All these units, however, have one feature in common, namely, a more or less flat lamellar shape. The mean values of ring condensation index and aromaticity and the dimensions of the condensed aromatic nuclei of the lamellae, as well as the number and character of the functional groups in the molecular periphery, can be derived from the results of structural analysis.

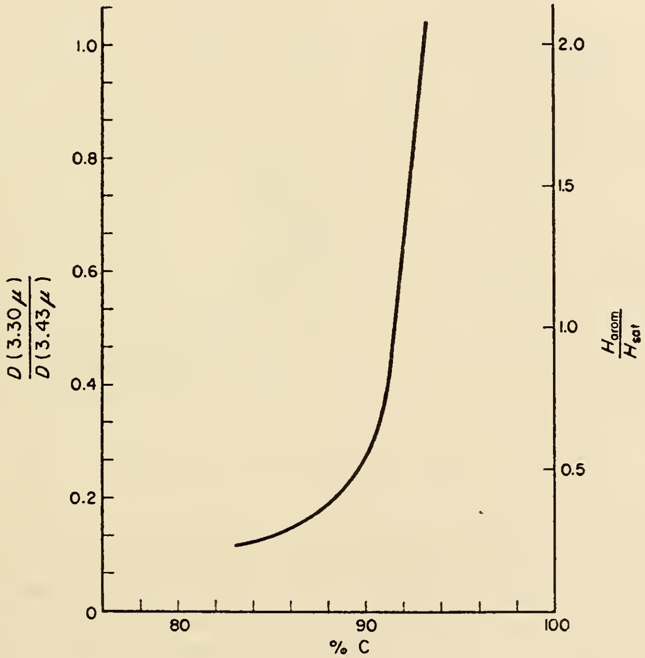


FIG. 51. Functional hydrogen groups (optical density ratio).

When coalification starts, the aromatic clusters are still relatively small and are probably connected by non-aromatic bridges. This explains why the lowest rank coals possess a pronounced polymeric character and more or less open structure. From a chemical point of view, coalification must be considered as a process in which the degree of condensation and aromaticity of the starting material increase continuously; the bridge structures become unstable as the interaction forces between the aromatic nuclei grow stronger. On continued coalification, the polymeric structure, in which not only covalent bridges but also interactions between the polar groups play an important part, is modified into what, based on X-ray studies, has become known as the "liquid" structure. This structure is typical of coking coal. Subsequently, the structure stiffens again (anthracitization) and the lamellae display a growing tendency for orientation parallel to the bedding plane.

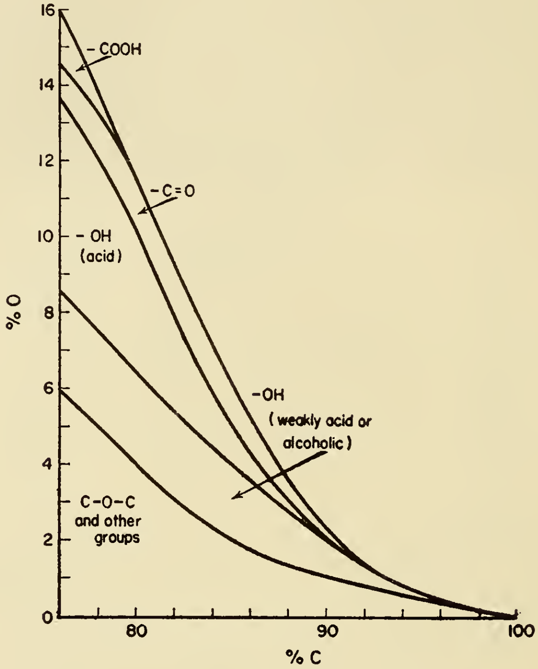


FIG. 52. Functional oxygen groups (vitrinites).

The tendency of the flat lamellae to coalesce into small stacks, the crystallites in the X-ray diagram, can be observed in all terms of the coalification series and this phenomenon becomes more marked as coalification advances. The inter- (and intra- ?) lamellar holes together constitute the ultra micro-pore system and are responsible for the adsorption, solvent-interaction, and swelling effects.

In a qualitative respect this also holds for the other macerals, with the understanding that as far as aromaticity, ring condensation index, and cluster dimensions are concerned, exinites always lag behind vitrinites of the same rank, whereas micrinites have advanced further (Dormans *et al.*, 1957; Kröger, 1956; Kröger *et al.*, 1957a–g). The physical and chemical properties of coal can be interpreted in the light of this structural picture.

The mechanical properties of coal result from the various contributions to its cohesion. During coalification the originally small aromatic clusters with their covalent (but flexible ?) bridges and weak interaction forces increase in size, and interaction grows stronger while part of the bridges disappear. The minimum in cohesion, and hence in mechanical strength, is the result of these two antagonistic cohesion forces. Beyond this minimum, in the anthracite range, the mechanical strength increases with rank. The bulk modulus (reciprocal compressibility), for example, is directly proportional to the size of the clusters (van Krevelen and Schuyer, 1957).

The cluster model also provides a natural explanation of the electrical and thermal properties. Semi-conductance is an intrinsic property of extensive condensed aromatic systems, and its temperature dependence varies with the size of the aromatic clusters.

The dielectric constant in the range of true coking coal appears to be equal to the square of the refractive index, which is in accord with the theory for non-polar insulators; coals of this rank possess a vitreous structure. Other coals have a higher dielectric constant either because of the presence of peripheral polar groups (low-rank coals) or to the effect of semiconductance (high-rank coals).

The coefficient of thermal expansion shows the expected behavior: parallel to the bedding plane a gradual decrease with increasing rank, and perpendicular to the bedding plane a strong decrease in the anthracite stage. The latter is accompanied by a peculiar anisotropy effect, possibly caused by the orientation and subsequent disappearance of the pore system.

The specific heat of coal has been fully accounted for by the rigid structure of the lamellae. It may be assumed that at normal temperatures on the average only one degree of freedom will be available in every atom. The values of specific heat calculated on the basis of this assumption agree well with the experimental data (see van Krevelen and Schuyer, 1957).

The properties of coal on heating can also be explained simply by means of the structural model. Heating to temperatures beyond 300°C causes thermal cracking with the result that the aromatic clusters, which are wholly or partly present in the polymerized form, begin to appear as free units (free radicals). As long as the aromatic clusters are sufficiently small and have a sufficiently long lifetime, the fragments are mobile giving the coal a plastic character. Low-rank coals, however, do not soften because, although cracking is complete, the lifetime of the radicals is too short (high reactivity). In the case of high-rank coals the cracking yield is small and the interaction between the aromatic clusters so strong that no softening can occur. Softening, therefore, can only occur in a limited range of rank.

The variation in volatile matter content with rank can also be understood from the structural picture. Only the smallest aromatic clusters will become volatile on heating, the majority forming the coke residue. This implies that there must exist a distinct relationship between aromaticity and volatile matter content, these two quantities more or less complementing each other. The large differences between the various macerals with regard to behavior on heating can be immediately understood from the constitutional parameters. Micrinites, with their relatively large aromatic clusters and high aromaticity, do not soften; exinites (particularly in low-rank coals), with their low aromaticity and small aromatic clusters, form the opposite extreme and leave only little coke residue. Vitrinites, as usual, come midway between the two. Analogous reasoning holds for the hydrogenolysis process. Hydrogenation of the macerals is possible unless the size of the clusters exceeds a given limit. This explains why micrinites of relatively low rank cannot be hydrogenated, whereas hydrogenation of exinites and vitrinites remains possible as long as they are capable of softening on heating. The oils obtained by hydrogenolysis are highly cyclic.

Finally there is the oxidation of coal by molecular oxygen. The formation and structure of "humic acids" can be interpreted as a rupturing of the peripheral ring systems with simultaneous formation of anhydride groups which, on hydrolysis with alkalis, are transformed into acid groups (—COOH and —OH). The fact that low-rank coals are particularly subject to oxidation (low activation energy) is also consistent with the concept of an "open" polymeric structure as well as with the fact that the non-aromatic fraction of the molecule is relatively important and may contain tertiary hydrogen atoms.

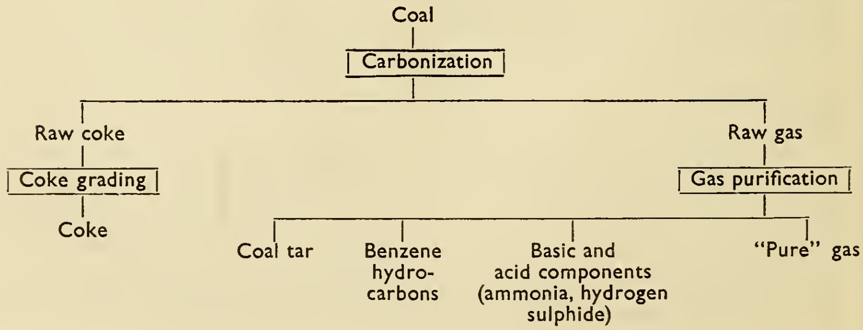
Our present structural model, although it cannot be expressed in a structural formula, provides a qualitative explanation of virtually all, and a quantitative explanation of some of the properties of coal.

Coal Utilization (Lowry, 1945; Brown, 1956; Townsend, 1956)

The principal technical applications of coal are its complete conversion into heat (*combustion*) and its conversion into other, secondary, fuels. Only the latter type of conversions, including *carbonization*, *gasification* and *hydrogenation*, will be briefly dealt with in the following pages.

The most important chemical conversion of coal is the *carbonization* process, i.e. the production of coke and gas. The total amount of coal carbonized in coking plants and gas works all over the world is about 200 million tons a year. Carbonization is a thermal cracking process by which coal is transformed as shown in the following diagram:

DIAGRAM 4



The structural model of coal permits a mental picture to be formed of what happens in the carbonization process: the side chain and peripheral groups are detached from the aromatic clusters by cracking and evolve as "gas", following which the clusters recondense to carbon (coke). As a gross process, carbonization may be visualized as a *disproportionation* into one product with a high, and one with a low, hydrogen content. Fragments of the molecule having a low enough molecular weight evaporate, undergo secondary cracking by the hot coke, and finally recondense to tar.

The products resulting from this drastic decomposition are, on the one hand, coke, water gas, producer gas and synthesis gas, and on the other hand, a variety of very valuable chemical basic compounds, materials of low molecular weight such as the whole series of benzene hydrocarbons, hydrogen (starting material for the ammonia synthesis and hydrogenation processes), and ethylene (starting material for the production of alcohol, ether, polyethylene, glycol, vinyl compounds, etc.). The heavy chemical industry and public gas supplies are partly based on the processing of materials obtained by carbonization of coal.

The second process, *gasification*, that is the complete conversion of coal to gas, is mainly carried out in two stages: coke production followed by coke gasification. The present state of technology, however, has made it possible to convert coal, by reaction with steam and oxygen, directly and completely into high-grade gas that may be used as city gas, and also to prepare synthesis gas from coal by a direct process. From a chemical point of view, gasification is to be considered the most drastic disintegration of coal: break-down into its most simple components: CO, H_2 and H_2O. Extensive installations for the direct gasification of coal have already been built, for example in South Africa, where the gas is used for the production of synthetic oils by the Fischer–Tropsch process. This process has opened the whole field of aliphatic organic chemistry to coal technology; its realization, however, is only economically justified in those areas where coal can be obtained at an extremely low price.

The third process, *hydrogenation*, in contrast to the other major technical processes, leaves the coal molecule fairly intact. The coal molecule is first broken down into fragments, which, however, being saturated with hydrogen, cannot disproportionate further. By heating the coal with hydrogen to about 400°C under high pressure, hydrocarbons of widely differing boiling range are obtained. These are gases, petroleum, and light, medium, and heavy oils. During the war very large quantities of coal and brown coal were hydrogenated, especially in Germany where the total rate of conversion was 4 million tons/year. The development of the hydrogenation process has provided a means to transform coal into petroleum and thus to profit from all the technical possibilities afforded by this achievement. Unfortunately, the price of hydrogen is so high that hydrogenation of coal is not yet an economic proposition.

A few other chemical conversion processes of some industrial importance, which leave the coal molecule largely intact, are based on reaction of coal with oxygen or sulphur trioxide. Owing to the introduction of polar groups (–OH, –COOH, $-SO_3H$) by these agents, the coal acquires ion-exchange properties.

As a basic chemical material, coal is in a position analogous to mineral oil: it is mainly the low molecular weight decomposition products of simple chemical composition that constitute the starting materials for the chemical industry. The products derived from them, however, are so indispensable and of such a versatility that it is fully justified to speak of the chemical value of coal.

Coal Classification—The term "coal classification" denotes the arrangement of coal into types, mainly according to the various fields of application.

The oldest classification system, drawn up by Regnault (1837), was based on the oxygen content. In Seyler's system (1900, 1901, 1931, 1938) the carbon and hydrogen contents are used as parameters. As the relationship between elementary composition and technological properties is a complicated one, however, attempts have been made to use the technological properties themselves as classification parameters.

In all countries the classification systems used are primarily based on the content of volatile matter (see Figs. 53–60). Broadly speaking, the classes distinguished in these systems are alike. Coals with less than about 10% of volatile matter are called anthracite. The next class, about 10 to 13% volatile matter, is called lean coal in some countries and semi-anthracite in others (in Great Britain, dry-steam coal). Next comes a transition class whose name differs from country to country, and which contains from about 14 to 20% of volatile matter. The group with about 20 to 30% volatile matter is mostly called "fat" or coking coal. Above 30% the coal is hard to classify on the basis of volatile matter alone and usually other quantities have to be included in the classification.

A few countries, namely Germany, The Netherlands, and Czechoslovakia, have adopted a purely qualitative classification for the latter coals. This system is based on the appearance of the coke button obtained in the determination of the content of volatile matter.

A second parameter is being used in other countries. For example, the United States chose the calorific value for this purpose. All coals containing more than 31% of volatile matter are classified according to this principle. A difficulty encountered in the classification of these coals is that the calorific value on the basis of dry and mineral matter-free coal permitted too small a differentiation to enable the large numbers of United States coals of this type, with their large differences in quality, to be accurately classified. For this reason it was decided to make use of the moisture content of the coal at a temperature of 30°C and a relative humidity of 97%. The latter quantity corresponds more or less to the natural moisture content of the coal seam, and the calorific value is given on the basis of mineral matter-free coal with a moisture content,

Fig. 53 **Belgium**

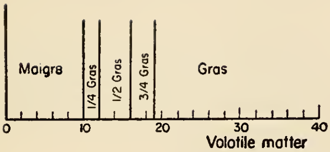


Fig. 54 **Germany**

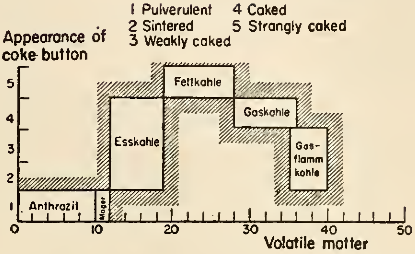


Fig. 55 **The Netherlands**

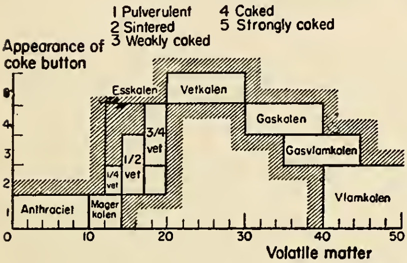


Fig. 56 **France**

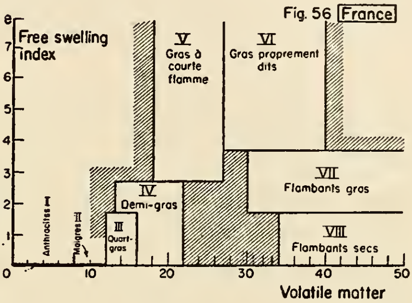


Fig. 57 **Italy**

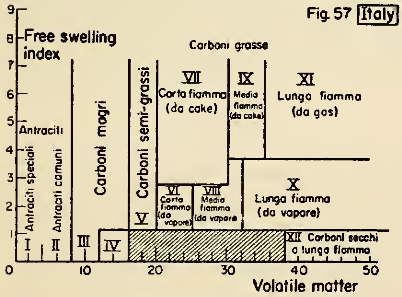


Fig. 58 **Poland**

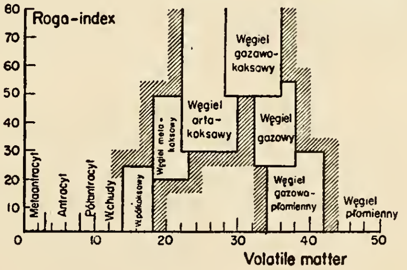


Fig. 59 **United Kingdom**

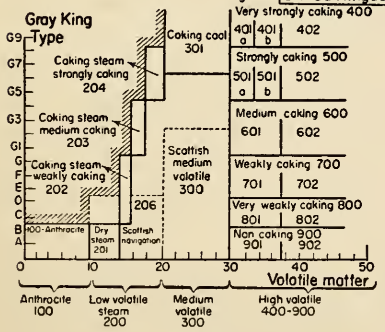
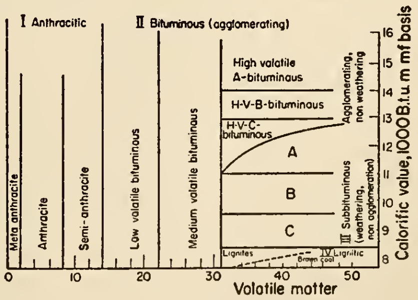


Fig. 60 **U.S.A.**



FIGS. 53–60. Commercial classification systems.

equal to that of the coal under natural conditions. Coals with more than 31% of volatile matter can, on this basis, be classified into 3 groups: high volatile bituminous coal, subbituminous coal (formerly black lignites) and lignite. Each of these groups is differentiated into several subdivisions (Fig. 60).

In other countries where coal classification has been standardized, either the caking or the coking properties are used as second parameter.

In Great Britain, the National Coal Board has adopted the Gray–King assay as parameter for the caking properties (Fig. 59). A drawback attached to this system is that the identification of a coal takes much time owing to the long duration of the Gray–King assay.

In France, the swelling index has been adopted as second parameter (Fig. 56). This is a rapid determination but the results only supply information on the behavior of coal on rapid heating in a fuel bed, but not on its coking properties. A slightly modified version of the French system is used (Fig. 57) in Italy.

Poland has accepted the *Roga* test as second parameter. The classification in use there involves the danger that the classes may overlap each other (Fig. 58).

The foregoing shows that in all countries the original classification of coal has been elaborated on practically the same principles. However, when the need was felt for a more detailed differentiation and a second parameter was being included in the classification, the various countries started to follow different lines. This fact accounts for the present lack of clear correlation between the classification systems of the main coal producing countries.

International Coal Classification

After World War II the United Nations stimulated the development of an international coal classification system. In this system, worked out by the Coal Committee of the E.C.E. in Geneva (1956), the volatile matter content on the basis of dry and mineral matter-free coal was chosen as a main parameter. However, this criterion only permits an unambiguous interpretation if the coal concerned contains less than 33% volatile matter. For coals with more than 33% volatile matter, the rank of the coal is expressed in terms of its calorific value, and more specifically in terms of the gross calorific value on the basis of mineral matter-free coal which at 30°C is in equilibrium with air with a relative humidity of 97%. The American standard, calorific value calculated to the dry and mineral matter-free substance, permits too little differentiation. With the aid of these rank parameters coal can be classified into several classes.

As a second parameter, the Committee chose an index denoting the caking properties on rapid heating; this parameter consequently characterizes the behavior of coal on a grate. It has already been noted that the determination of the *swelling index* and the *Roga index* are the best reproducible methods available for this purpose. The sub-division of the coal classes into groups on the basis of the caking power is as follows:

Group	Caking properties	Swelling index	*Roga* index
0	none	NA*	0–5
1	weak	1–2	5–20
2	medium	2.5–4	20–45
3	strong	>4	>45

* Non-agglomerating.

This division shows a fairly close resemblance to the system used in France, Italy and Poland, as well as to the more qualitative methods of The Netherlands and Germany.

In addition to obtaining a measure of the caking properties on rapid heating, it was also essential to find a criterion for determining the suitability of coal for the manufacture of coke. Great Britain had already taken the lead in the search for such a criterion. In the system introduced by the National Coal Board, the results of the Gray–King assay are used as a measure of the coking properties. As the Gray–King assay and the dilatometer test according to Audibert–Arnu show a good correlation, these tests may be used alternately. The coking properties, therefore, constitute the third parameter for dividing the classes into sub-groups. On the analogy of the British system, the limits between these sub-groups have been fixed as follows:

Sub-groups	Coking properties	Dilatometer test (% dilatation)	Gray–King test (coke type)
0	none	no softening	A
1	poor (only to be used as an addition to coal with excessive coking properties)	contraction only	B–D
2	weak (only to be used as an addition to coals with very good coking properties)	$\geqslant 0$	E–G
3	moderate (preferably to be blended)	0–50	G_1–G_4
4	good	50–140	G_5–G_8
5	excessive (to be blended with coal with poorer coking properties)	>140	$>G_8$

TABLE 2. *International Classification of Hard Coals by Type*
(Coals with gross calorific value over 5,700 kcal/kg on moist, ash-free basis)

GROUPS (determined by caking properties)			CODE NUMBERS										SUB-GROUPS (determined by coking properties)		
Group number	Alternative group parameters		The first figure of the code number indicates the class of the coal, determined by volatile matter content up to 33% V.M. and by calorific parameter above 33% V.M. The second figure indicates the group of coal, determined by caking properties. The third figure indicates the sub-group, determined by coking properties.										Sub-group number	Alternative sub-group parameters	
	Crucible-swelling number	*Roga* index												Dilatometer	Gray–King
3	>4	>45					435	535	635				5	>140	>G8
						334	434	534	634				4	>50–140	G5–G8
						333	433	533	633	733			3	>0–50	G1–G4
						332 a 332 b	432	532	632	732	832		2	⩽0	E–G
2	2½–4	>20–45				323	423	523	623	723	823		3	>0–50	G1–G4
						322	422	522	622	722	822		2	⩽0	E–G
						321	421	521	621	721	821		1	Contraction only	B–D
1	1–2	>5–20			212	312	412	512	612	712	812		2	⩽0	E–G
					211	311	411	511	611	711	811		1	Contraction only	B–D
0	0–½	0–5		100 A B	200	300	400	500	600	700	800	900	0	Non-softening	A
Class number →			0	1	2	3	4	5	6	7	8	9			
Class parameters	Volatile matter (d.a.f.) →		0–3	>3–10 >3–6.5 >6.5–10	>10–14	>14–20	>20–28	>28–33	>33	>33	>33	>33			
	Calorific parameter*		—	—	—	—	—	—	>7 750	>7 200–7 750	>6 100–7 200	>5 700–6 100			

As an indication, the following classes have an approximate volatile matter content of:
Class 6 . . . 33–41%
7 . . . 33–44%
8 . . . 35–50%
9 . . . 42–50%

CLASSES
(determined by volatile matter up to 33% V.M. and by calorific parameter above 33% V.M.)

NOTE.—(i) Where the ash content of coal is too high to allow classification according to the present systems, it must be reduced by laboratory float-and-sink method (or any other appropriate means). The specific gravity selected for flotation should allow a maximum yield of coal with 5 to 10% of ash.
(ii) 332a . . . >14–16% V.M. 332b . . . >16–20% V.M.

* Gross calorific value on moist, ash-free basis (30°C, 96% humidity) kcal/kg.

The code figures of the classes, groups and sub-groups may be combined into a three-figure code number, the first figure indicating the class, the second the group, and the third the sub-group. In this way a decimal code is obtained.

The resulting classification system is shown in Table 2. In this table the theoretical number of possible classes has already been reduced and adapted to the principal existing varieties of coal. Finally, a number of the sub-groups of this comprehensive classification system have, for statistical purposes, been combined into the groupings I–VII.

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CHAPTER 7

GEOCHEMISTRY OF PETROLEUM*

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THE first commercial production of petroleum from wells in 1859, rapidly followed by development of the new petroleum industry in Pennsylvania, West Virginia, Ohio, Ontario, and Russia, attracted the keen attention of geologists and chemists to the nature and origin of this substance and its fluid components, crude oil and natural gas. Earliest observation had established the migratory nature of these fluids, largely hydrocarbons, in the porous and permeable rocks in which they are found. In legal decisions, judges sought a similar kind of property in ancient English common law, and chose the right of possession after capture of wild animals while within the bounds of landed property; and thus, oil and gas were called fugitive substances. This law of capture is still the basis of petroleum law governing property rights affected by movement of oil and gas during flow toward wells.

Geologists, searching for sedimentary formations rich in organic remains, found such beds not in the porous and permeable sandstones, common petroleum reservoirs, but in adjacent argillites and shales. Therefore, they inferred the origin of crude oil and natural gas to have been in the organic beds at some ancient geological time, after sedimentary deposition in the sea inasmuch as the fossil organic remains were marine. Consequent migration was called upon to bring the petroleum to the reservoir. First proposal of such source and process of concentration came in 1866 from Lesquereux, soon to be followed by similar suggestions by Newberry, Orton and White.

Chemists, in experiments summarized by Engler and von Höfer (1913–1925) and Clarke (1924), attempted to produce the hydrocarbons of petroleum in the laboratory from oils and fats derived from living organisms, both animal and vegetable. These syntheses, usually conducted at a high temperature, lacked the control imposed by geological conditions later known from the study of oil field temperatures and pressures, and today are chiefly of historical interest (Cox, 1946; Levorsen, 1954).

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* Chapter revised in 1962.

Organized research on the source of petroleum began with the research projects of the American Petroleum Institute. First research under this sponsorship, by Heald (1943), failed to contribute significantly to the desired end. Trask (1932), as part of American Petroleum Institute Research Project 4 on recent sediments, recorded analyses from many and varied environments of marine sedimentation. Later research on ancient sediments, carried out by him in this project, lasted until 1940. This research was followed by American Petroleum Institute sponsorship from 1942 to 1958 of studies of the transformation of the organic substances of marine sediments into the hydrocarbons of petroleum. Finally, similar sponsorship resulted in excellent research on recent sedimentation on the Gulf Coast of Louisiana and Texas.

With the establishment of geological research laboratories by petroleum companies in the last 2 decades, and with further sponsorship of research by the industry in academic institutions, investigation of the nature of petroleum and of its source has been extended. The term geochemistry, however, has only recently been used to designate this type of work. Bonham (1956) restricted his "geochemical investigation of crude oils" to the trace metals in the oils, inasmuch as crude oil in the field tank is only a part, although a great part, of the petroleum in the underground reservoir. In the present discussion of the subject a broader scope of the term "geochemistry of petroleum" is suggested, consideration is given to organic source substances, to both physical and chemical processes effecting changes in source materials in the source beds, during migration, and in the reservoir, and to the chemical characteristics of both organic and metallic components in the reservoir fluid, petroleum. The geochemistry of petroleum in this sense is largely organic geochemistry.

Correlative to the geochemistry of petroleum itself are other aspects of geochemistry. The source sediment and its environment, the organic sediments other than definitively proved source beds of petroleum, and the broad characteristics of what has been called the "habitat of oil" (Weeks, 1958) are all of primary interest in relation to petroleum.

Organic Constituents of Crude Oil

Development of modern techniques has permitted the isolation and absolute identification of many of the constituents of crude oil. Early work showed the need for fractional distillation equipment of high efficiency, chromatographic procedures were later introduced for separation of aromatic compounds, and in the past few years gas–liquid chromatography has appeared on the scene as a relatively simple, rapid, and accurate technique for separation, identification, and quantitative determination of the constituents of crude oil.

Crude oil may be defined as a naturally occurring complex mixture of hydrocarbons with small or trace quantities of oxygen-, sulfur-, or nitrogen-containing compounds and of metallic constituents. Some of these hydrocarbons may be very low-boiling, such as methane, in which case the compound may in part be dissolved in the crude oil, and may in part occur as associated gas. The occurrence of such a gaseous constituent depends upon the quantity present and its solubility in the oil. Although the gas associated with petroleum normally consists of methane, ethane, propane and butanes, some gases contain high-molecular-weight hydrocarbons in smaller quantities along with carbon dioxide and even nitrogen.

Analysis of crude oil was of concern to the petroleum industry for many years and resulted in the establishment, in 1927, of American Petroleum Institute Research Project 6 devoted initially to "The Separation, Identification and Determination of the Chemical Constituents of Commercial Petroleum Fractions". This study was established at the National Bureau of Standards in Washington, D.C. and used, as a representative sample, crude oil from the Brett No. 6 well of the Ponca City field, Oklahoma (Rossini, Mair, and Streiff, 1953). Later, the objectives of the project were expanded to include synthesis of pure hydrocarbons for comparison with those isolated from the oil.

By 1953 nearly 130 hydrocarbons had been separated from the Ponca City crude oil and positively identified; since that time, additional compounds have been identified. Other laboratories in various countries have also contributed both qualitative and quantitative data on hydrocarbons isolated from a variety of types of crude oil. Russian, Chinese, Iranian, and Near Eastern oils, among others, have all been examined in considerable detail. In Table 1 are listed over 200 hydrocarbons known to occur in various crude oils along with quantitative data, where available. The tremendous variety of compounds illustrates the complexity of the mixture, especially inasmuch as these compounds, based on quantitative considerations, probably account for well under 50% of the constituents of a crude petroleum.

The compounds thus far isolated from crude oil are rather simple and include basic paraffinic, cycloparaffinic, and aromatic types. A few more complicated multiple-ring structures, such as adamantane and some bicyclooctanes, have also been identified, but the complex structures of the lubricating oil fraction can only be described in very general terms. Here, where the compounds may be composed of mixed aromatic, cycloparaffinic, and paraffinic structures, the number of possible compounds becomes almost infinitely large and the likelihood of positive identification of any one becomes vanishingly small. For this reason, higher-boiling fractions of crude oil are characterized by their physical properties, which provide a clue as to the ratios of the aromatic, cycloparaffinic, and paraffinic structures that are present. Thus, it is possible to estimate an average number of aromatic and cycloparaffinic rings and of paraffinic chains per molecule. The tremendous number of isomeric structures having similar physical properties that are possible for such compounds, makes it unlikely that any appreciable number of them will ever be isolated and positively identified.

TABLE 1

Hydrocarbons Identified in Crude Oil

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
CH_4	Methane	−161.49	Paraffin	All crude oils	—	8
C_2H_6	Ethane	− 88.63	Paraffin	Ponca City, Okla.	—	8
				Saudi Arabia	0.03	116
				El Dorado Comp.	0.01	116
				Kuwait	—	116
				Wyoming Comp.	0.01	116
				Beaver Lodge (N. Dak.)	0.04	116
				Tia Juana (Venezuela)	0.02	116
				Teas (Tex.)	0.04	116
				Winkler (Tex.)	0.02	116
				W. Kansas Comp.	0.02	116
				Eola (Okla.)	0.03	116
				Beaver Lodge (N. Dak.)	0.03	116
				Texas	0.01	116
				Alida (S.E. Sask., Can.)	0.04	116
				Langunillas Quince (Venezuela)	0.037	116
				Redwater (Edmonton, Can.)	0.08	116
				Lee-Harrison (Tex.)	0.03	116
				North Smyer (Tex.)	0.06	116
				Hastings (Tex.)	0.004	116
				Wilmington (Cal.)	0.004	116
				South Houston (Tex.)	0.004	116
				Mid-Continent Comp. (U.S.A.)	0.010 ± 0.001	116

* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_3H_8	Propane	−42.07	Paraffin	Ponca City, Okla.	—	8
				Saudi Arabia	0.010	116
				El Dorado Comp.	0.018	116
				Kuwait	—	116
				Wyoming Comp.	0.12	116
				Beaver Lodge (N. Dak.)	0.37	116
				Tia Juana (Venezuela)	0.18	116
				Teas (Tex.)	0.25	116
				Winkler (Tex.)	0.053	116
				W. Kansas Comp.	0.21	116
				Eola (Okla.)	0.41	116
				Beaver Lodge (N. Dak.)	0.26	116
				Texas	0.19	116
				Alida (S.E. Sask., Can.)	0.35	116
				Lagunillas Quince (Venezuela)	0.036	116
				Redwater (Edmonton, Can.)	0.69	116
				Lee-Harrison (Tex.)	0.21	116
				North Smyer (Tex.)	0.69	116
				Hastings (Tex.)	0.037	116
				Wilmington (Cal.)	0.034	116
				South Houston (Tex.)	0.040	116
				Mid-Continent Comp. (U.S.A.)	0.179 ± 0.003	116
C_4H_8	Cyclobutane		Cycloparaffin	Bachaquero, W. Venezuela	0.001	117
C_4H_{10}	*n*-Butane	− 0.50	Paraffin	Ponca City, Okla.	—	8
				Saudi Arabia	0.96	116
				El Dorado Comp.	1.40	116

C_4H_{10}	*n*-Butane	— 0.50	Paraffin	Kuwait	0.027	116
				Wyoming Comp.	0.38	116
				Beaver Lodge (N. Dak.)	1.02	116
				Tia Juana (Venezuela)	0.47	116
				Teas (Tex.)	2.16	116
				Winkler (Tex.)	0.20	116
				W. Kansas Comp.	0.75	116
				Eola (Okla.)	1.07	116
				Beaver Lodge (N. Dak.)	0.82	116
				Texas	2.54	116
				Alida (S.E. Sask., Can.)	1.11	116
				Lagunillas Quince (Venezuela)	0.85	116
				Redwater (Edmonton, Can.)	1.43	116
				Lee-Harrison (Tex.)	0.58	116
				North Smyer (Tex.)	1.69	116
				Hastings (Tex.)	0.40	116
				Wilmington (Cal.)	0.134	116
				South Houston (Tex.)	0.090	116
				Mid-Continent Comp. (U.S.A.)	0.83 ± 0.01	116
C_4H_{10}	*iso-Butane*	— 11.73	Paraffin	Ponca City, Okla.	—	8
				Saudi Arabia	0.14	116
				El Dorado Comp.	0.36	116
				Kuwait	0.001	116
				Wyoming Comp.	0.12	116
				Beaver Lodge (N. Dak.)	0.31	116
				Tia Juana (Venezuela)	0.15	116
				Teas (Tex.)	0.43	116
				Winkler (Tex.)	0.050	116
				W. Kansas Comp.	0.18	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_4H_{10}	*iso-Butane*	− 11.73	Paraffin	Eola (Okla.)	0.30	116
				Beaver Lodge (N. Dak.)	0.23	116
				Texas	0.90	116
				Alida (S.E. Sask., Can.)	0.24	116
				Lagunillas Quince (Venezuela)	0.046	116
				Redwater (Edmonton, Can.)	0.43	116
				Lee-Harrison (Tex.)	0.19	116
				North Smyer (Tex.)	0.33	116
				Hastings (Tex.)	0.041	116
				Wilmington (Cal.)	0.033	116
				South Houston (Tex.)	0.039	116
				Mid-Continent Comp. (U.S.A.)	0.188 ± 0.002	116
C_5H_{10}	Cyclopentane	49.26	Cycloparaffin	Ponca City, Okla.	0.05	9
				Saudi Arabia	0.083	116
				El Dorado Comp.	0.085	116
				Kuwait	0.040	116
				Wyoming Comp.	0.058	116
				Beaver Lodge (N. Dak.)	0.13	116
				Tia Juana (Venezuela)	0.081	116
				Teas (Tex.)	0.18	116
				Winkler (Tex.)	0.048	116
				W. Kansas Comp.	0.095	116
				Eola (Okla.)	0.15	116
				Beaver Lodge (N. Dak.)	0.18	116
				Texas	0.20	116
				Alida (S.E. Sask., Can.)	0.16	116
				Lagunillas Quince (Venezuela)	0.029	116

C_5H_{10}	Cyclopentane	49.26	Cycloparaffin	Redwater (Edmonton, Can.)	0.14	116
				Lee-Harrison (Tex.)	0.11	116
				North Smyer (Tex.)	0.32	116
				Hastings (Tex.)	0.095	116
				Wilmington (Calif.)	0.054	116
				South Houston (Tex.)	0.033	116
				Mid-Continent Comp. (U.S.A.)	0.105 ± 0.003	116
C_5H_{12}	2,2-Dimethylpropane	9.50	Paraffin	Ponca City, Okla.	—	45
				Refinery stream	—	101
				Saudi Arabia	0.008	116
				El Dorado Comp.	0.017	116
				Kuwait	0.000	116
				Wyoming Comp.	0.007	116
				Beaver Lodge (N. Dak.)	0.004	116
				Tia Juana (Venezuela)	0.002	116
				Teas (Tex.)	0.006	116
				Winkler (Tex.)	0.002	116
				W. Kansas Comp.	0.005	116
				Eola (Okla.)	0.005	116
				Beaver Lodge (N. Dak.)	0.002	116
				Texas	0.030	116
				Alida (S.E. Sask., Can.)	0.005	116
				Lagunillas Quince (Venezuela)	0.001	116
				Redwater (Edmonton, Can.)	0.003	116
				Lee-Harrison (Tex.)	0.005	116
				North Smyer (Tex.)	0.008	116
				Hastings (Tex.)	0.010	116
				Wilmington (Calif.)	0.000	116
				South Houston (Tex.)	0.002	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_5H_{12}	2,2-Dimethylpropane	9.50	Paraffin	Mid-Continent Comp. (U.S.A.)	0.000	116
				Western Venezuela	0.003	117
C_5H_{12}	2-Methylbutane	27.85	Paraffin	Ponca City, Okla.	0.5	8, 45
				Saudi Arabia	0.73	116
				El Dorado Comp.	1.44	116
				Kuwait	0.16	116
				Wyoming Comp.	0.54	116
				Beaver Lodge (N. Dak.)	0.99	116
				Tia Juana (Venezuela)	0.56	116
				Teas (Tex.)	1.54	116
				Winkler (Tex.)	0.35	116
				W. Kansas Comp.	0.62	116
				Eola (Okla.)	0.94	116
				Beaver Lodge (N. Dak.)	0.83	116
				Texas	1.85	116
				Alida (S.E. Sask., Can.)	0.84	116
				Lagunillas Quince (Venezuela)	0.128	116
				Redwater (Edmonton, Can.)	1.02	116
				Lee-Harrison (Tex.)	0.86	116
				North Smyer (Tex.)	1.35	116
				Hastings (Tex.)	0.53	116
				Wilmington (Calif.)	0.141	116
				South Houston (Tex.)	0.110	116
				Mid-Continent Comp. (U.S.A.)	0.64 ± 0.01	116
C_5H_{12}	*n*-Pentane	36.07	Paraffin	Ponca City, Okla.	—	8
				Saudi Arabia	1.42	116

C_5H_{12}	*n*-Pentane	36.07	Paraffin	El Dorado Comp.	1.47	116
				Kuwait	0.40	116
				Wyoming Comp.	0.52	116
				Beaver Lodge (N. Dak.)	1.58	116
				Tia Juana (Venezuela)	0.75	116
				Teas (Tex.)	2.30	116
				Winkler (Tex.)	0.20	116
				W. Kansas Comp.	1.07	116
				Eola (Okla.)	1.35	116
				Beaver Lodge (N. Dak.)	1.24	116
				Texas	2.17	116
				Alida (S.E. Sask., Can.)	1.41	116
				Lagunillas Quince (Venezuela)	0.129	116
				Redwater (Edmonton, Can.)	1.18	116
				Lee-Harrison (Tex.)	0.78	116
				North Smyer (Tex.)	1.68	116
				Hastings (Tex.)	0.51	116
				Wilmington (Cal.)	0.169	116
				South Houston (Tex.)	0.118	116
				Mid-Continent Comp. (U.S.A.)	1.12 ± 0.01	116
C_6H_6	Benzene	80.10	Aromatic	Ponca City, Okla.	0.15	12, 9
				Western Nesbit-Dag, Russia	—	47
				Saudi Arabia	0.11	116
				El Dorado Comp.	0.30	116
				Kuwait	0.053	116
				Wyoming Comp.	0.034	116
				Beaver Lodge (N. Dak.)	0.25	116
				Tia Juana (Venezuela)	0.094	116
				Teas (Tex.)	0.087	116

* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_6H_6	Benzene	80.10	Aromatic	Winkler (Tex.)	0.014	116
				W. Kansas Comp.	0.056	116
				Eola (Okla.)	0.19	116
				Beaver Lodge (N. Dak.)	0.27	116
				Texas	1.26	116
				Alida (S.E. Sask., Can.)	0.17	116
				Lagunillas Quince (Venezuela)	0.018	116
				Redwater (Edmonton, Can.)	0.068	116
				Lee-Harrison (Tex.)	1.01	116
				North Smyer (Tex.)	0.18	116
				Hastings (Tex.)	0.084	116
				Wilmington (Calif.)	0.015	116
				South Houston (Tex.)	0.037	116
				Mid-Continent Comp. (U.S.A.)	0.050 ± 0.001	116
C_6H_{12}	Methylcyclopentane	71.81	Cycloparaffin	Ponca City, Okla.	0.87	13, 9
				Makhachkala, Russia	0.36–0.49	48
				Saudi Arabia	0.27	116
				El Dorado Comp.	0.35	116
				Kuwait	0.19	116
				Wyoming Comp.	0.20	116
				Beaver Lodge (N. Dak.)	0.57	116
				Tia Juana (Venezuela)	0.33	116
				Teas (Tex.)	1.02	116
				Winkler (Tex.)	0.29	116
				W. Kansas Comp.	0.48	116
				Eola (Okla.)	0.85	116
				Beaver Lodge (N. Dak.)	0.63	116

C_6H_{12}	Methylcyclopentane	71.81	Cycloparaffin	Texas	0.84	116
				Alida (S.E. Sask., Can.)	0.74	116
				Lagunillas Quince (Venezuela)	0.144	116
				Redwater (Edmonton, Can.)	0.94	116
				Lee-Harrison (Tex.)	0.51	116
				North Smyer (Tex.)	2.14	116
				Hastings (Tex.)	0.49	116
				Wilmington (Cal.)	0.31	116
				South Houston (Tex.)	0.21	116
				Mid-Continent Comp. (U.S.A.)	0.53 ± 0.01	116
C_6H_{12}	Cyclohexane	80.74	Cycloparaffin	Ponca City, Okla.	0.71	15, 9
				Saudi Arabia	0.19	116
				El Dorado Comp.	0.37	116
				Kuwait	0.16	116
				Wyoming Comp.	0.18	116
				Beaver Lodge (N. Dak.)	0.59	116
				Tia Juana (Venezuela)	0.28	116
				Teas (Tex.)	0.84	116
				Winkler (Tex.)	0.24	116
				W. Kansas Comp.	0.42	116
				Eola (Okla.)	0.38	116
				Beaver Lodge (N. Dak.)	0.70	116
				Texas	0.70	116
				Alida (S.E. Sask., Can.)	1.05	116
				Lagunillas Quince (Venezuela)	0.103	116
				Redwater (Edmonton, Can.)	0.38	116
				Lee-Harrison (Tex.)	0.76	116
				North Smyer (Tex.)	1.05	116
				Hastings (Tex.)	0.75	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_6H_{12}	Cyclohexane	80.74	Cycloparaffin	Wilmington (Cal.)	0.116	116
				South Houston (Tex.)	0.32	116
				Mid-Continent Comp. (U.S.A.)	0.43 ± 0.01	116
C_6H_{14}	2,2-Dimethylbutane	49.74	Paraffin	Ponca City, Okla.	0.04	9
				Saudi Arabia	0.007	116
				El Dorado Comp.	0.093	116
				Kuwait	0.005	116
				Wyoming Comp.	0.013	116
				Beaver Lodge (N. Dak.)	0.018	116
				Tia Juana (Venezuela)	0.011	116
				Teas (Tex.)	0.027	116
				Winkler (Tex.)	0.028	116
				W. Kansas Comp.	0.018	116
				Eola (Okla.)	0.008	116
				Beaver Lodge (N. Dak.)	0.010	116
				Texas	0.021	116
				Alida (S.E. Sask., Can.)	0.014	116
				Lagunillas Quince (Venezuela)	0.006	116
				Redwater (Edmonton, Can.)	0.010	116
				Lee-Harrison (Tex.)	0.007	116
				North Smyer (Tex.)	0.008	116
				Hastings (Tex.)	0.057	116
				Wilmington (Cal.)	0.002	116
				South Houston (Tex.)	0.222	116
				Mid-Continent Comp. (U.S.A.)	0.014 ± 0.002	116
C_6H_{14}	2,3-Dimethylbutane	57.99	Paraffin	Ponca City, Okla.	0.08	10, 9

C_6H_{14}	2,3-Dimethylbutane	57.99	Paraffin	Saudi Arabia	0.080	116
				El Dorado Comp.	0.18	116
				Kuwait	0.056	116
				Wyoming Comp.	0.068	116
				Beaver Lodge (N. Dak.)	0.12	116
				Tia Juana (Venezuela)	0.076	116
				Teas (Tex.)	0.138	116
				Winkler (Tex.)	0.078	116
				W. Kansas Comp.	0.072	116
				Eola (Okla.)	0.068	116
				Beaver Lodge (N. Dak.)	0.095	116
				Texas	0.14	116
				Alida (S.E. Sask., Can.)	0.10	116
				Lagunillas Quince (Venezeula)	0.030	116
				Redwater (Edmonton, Can.)	0.001	116
				Lee-Harrison (Tex.)	0.16	116
				North Smyer (Tex.)	0.091	116
				Hastings (Tex.)	0.11	116
				Wilmington (Cal.)	0.022	116
				South Houston (Tex.)	0.040	116
				Mid-Continent Comp. (U.S.A.)	0.074 ± 0.002	116
C_6H_{14}	2-Methylpentane	60.27	Paraffin	Ponca City, Okla.	0.37	10, 9, 11
				Makhachkala, Russia	—	48
				Saudi Arabia	0.64	116
				El Dorado Comp.	1.03	116
				Kuwait	0.36	116
				Wyoming Comp.	0.43	116
				Beaver Lodge (N. Dak.)	0.79	116
				Tia Juana (Venezuela)	0.48	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_6H_{14}	2-Methylpentane	60.27	Paraffin	Teas (Tex.)	0.96	116
				Winkler (Tex.)	0.28	116
				W. Kansas Comp.	0.52	116
				Eola (Okla.)	0.67	116
				Beaver Lodge (N. Dak.)	0.63	116
				Texas	0.90	116
				Alida (S.E. Sask., Can.)	0.79	116
				Lagunillas Quince (Venezuela)	0.111	116
				Redwater (Edmonton, Can.)	0.65	116
				Lee-Harrison (Tex.)	0.64	116
				North Smyer (Tex.)	1.20	116
				Hastings (Tex.)	0.29	116
				Wilmington (Cal.)	0.115	116
				South Houston (Tex.)	0.096	116
				Mid-Continent Comp. (U.S.A.)	0.52 ± 0.01	116
C_6H_{14}	3-Methylpentane	63.28	Paraffin	Ponca City, Okla.	0.35	10, 9, 11
				Makhachkala, Russia	0.64–0.77	48
				Saudi Arabia	0.46	116
				El Dorado Comp.	0.65	116
				Kuwait	0.30	116
				Wyoming Comp.	0.33	116
				Beaver Lodge (N. Dak.)	0.45	116
				Tia Juana (Venezuela)	0.31	116
				Teas (Tex.)	0.64	116
				Winkler (Tex.)	0.41	116
				W. Kansas Comp.	0.32	116
				Eola (Okla.)	0.47	116

C_6H_{14}	3-Methylpentane	63.28	Paraffin	Beaver Lodge (N. Dak.)	0.37	116
				Texas	0.61	116
				Alida (S.E. Sask., Can.)	0.54	116
				Lagunillas Quince (Venezuela)	0.072	116
				Redwater (Edmonton, Can.)	0.46	116
				Lee-Harrison (Tex.)	0.49	116
				North Smyer (Tex.)	0.83	116
				Hastings (Tex.)	0.19	116
				Wilmington (Cal.	0.098	116
				South Houston (Tex.)	0.070	116
				Mid-Continent Comp. (U.S.A.)	0.32 ± 0.01	116
C_6H_{14}	*n*-Hexane	68.74	Paraffin	Ponca City, Okla.	1.80	12, 9, 11
				Makhachkala, Russia	1.65–1.76	48
				Saudi Arabia	1.55	116
				El Dorado Comp.	1.67	116
				Kuwait	0.95	116
				Wyoming Comp.	0.66	116
				Beaver Lodge (N. Dak.)	2.03	116
				Tia Juana (Venezuela)	0.77	116
				Teas (Tex.)	1.70	116
				Winkler (Tex.)	0.23	116
				W. Kansas Comp.	1.11	116
				Eola (Okla.)	1.29	116
				Beaver Lodge (N. Dak.)	1.42	116
				Texas	1.35	116
				Alida (S.E. Sask., Can.)	1.49	116
				Lagunillas Quince (Venezuela)	0.143	116
				Redwater (Edmonton, Can.)	0.92	116
				Lee-Harrison (Tex.)	0.78	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_6H_{14}	*n*-Hexane	68.74	Paraffin	North Smyer (Tex.)	1.26	116
				Hastings (Tex.)	0.38	116
				Wilmington (Cal.)	0.135	116
				South Houston (Tex.)	0.110	116
				Mid-Continent Comp. (U.S.A.)	1.14 ± 0.01	116
C_7H_8	Toluene	110.62	Aromatic	Ponca City, Okla.	0.51	22, 9
				Western Nesbit-Dag, Russia	—	47
				Saudi Arabia	0.24	116
				El Dorado Comp.	0.34	116
				Kuwait	0.15	116
				Wyoming Comp.	0.12	116
				Beaver Lodge (N. Dak.)	0.76	116
				Tia Juana (Venezuela)	0.23	116
				Teas (Tex.)	0.30	116
				Winkler (Tex.)	0.093	116
				W. Kansas Comp.	0.083	116
				Eola (Okla.)	0.18	116
				Beaver Lodge (N. Dak.)	0.83	116
				Texas	0.99	116
				Alida (S.E. Sask., Can.)	1.02	116
				Lagunillas Quince (Venezeula)	0.052	116
				Redwater (Edmonton, Can.)	0.23	116
				Lee-Harrison (Tex.)	0.97	116
				North Smyer (Tex.)	0.19	116
				Hastings (Tex.)	0.13	116
				Wilmington (Cal.)	0.09	116
				South Houston (Tex.)	0.104	116

C_7H_{14}	Cycloheptane	118.79	Cycloparaffin	Ponca City, Okla.	0.01	8, 10
C_7H_{14}	1,1-Dimethylcyclopentane	87.85	Cycloparaffin	Ponca City, Okla.	0.16	16, 9
				Makhachkala, Russia	0.12–0.18	48
				Saudi Arabia	0.012	116
				El Dorado Comp.	0.044	116
				Kuwait	0.022	116
				Wyoming Comp.	0.030	116
				Beaver Lodge (N. Dak.)	0.059	116
				Tia Juana (Venezuela)	0.034	116
				Teas (Tex.)	0.092	116
				Winkler (Tex.)	0.081	116
				W. Kansas Comp.	0.073	116
				Eola (Okla.)	0.042	116
				Beaver Lodge (N. Dak.)	0.056	116
				Texas	0.081	116
				Alida (S.E. Sask., Can.)	0.090	116
				Lagunillas Quince (Venezuela)	0.018	116
				Redwater (Edmonton, Can.)	0.13	116
				Lee-Harrison (Tex.)	0.023	116
				North Smyer (Tex.)	0.22	116
				Hastings (Tex.)	0.070	116
				Wilmington (Calif.)	0.041	116
				South Houston (Tex.)	0.032	116
				Mid-Continent Comp. (U.S.A.)	0.077 ± 0.002	116
C_7H_{14}	1, *cis*-2-Dimethylcyclopentane	99.53	Cycloparaffin	Ponca City, Okla.	—	45
				Makhachkala, Russia	trace	48
				Saudi Arabia	0.0	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_7H_{14}	1, *cis*-2-Dimethylcyclopentane	99.53	Cycloparaffin	El Dorado Comp.	0.0	116
				Kuwait	0.03	116
				Wyoming Comp.	0.02	116
				Beaver Lodge (N. Dak.)	0.0	116
				Tia Juana (Venezuela)	0.05	116
				Teas (Tex.)	0.17	116
				Winkler (Tex.)	0.08	116
				W. Kansas Comp.	0.05	116
				Eola (Okla.)	0.18	116
				Beaver Lodge (N. Dak.)	0.0	116
				Texas	0.05	116
				Alida (S.E. Sask., Can.)	0.11	116
				Lagunillas Quince (Venezuela)	0.012	116
				Redwater (Edmonton, Can.)	0.22	116
				Lee-Harrison (Tex.)	0.03	116
				North Smyer (Tex.)	0.39	116
				Hastings (Tex.)	0.04	116
				Wilmington (Cal.)	0.04	116
				South Houston (Tex.)	0.02	116
				Mid-Continent Comp. (U.S.A.)	0.04	116
C_7H_{14}	1, *trans*-2-Dimethylcyclopentane	91.87	Cycloparaffin	Ponca City, Okla.	0.48	18, 9, 17
				Makhachkala, Russia	0.47–0.53	48
				Saudi Arabia	0.10	116
				El Dorado Comp.	0.12	116
				Kuwait	0.11	116
				Wyoming Comp.	0.15	116

C_7H_{14}	1, *trans*-2-Dimethylcyclopentane	91.87	Cycloparaffin	Beaver Lodge (N. Dak.)	0.18	116
				Tia Juana (Venezuela)	0.18	116
				Teas (Tex.)	0.51	116
				Winkler (Tex.)	0.17	116
				W. Kansas Comp.	0.32	116
				Eola (Okla.)	0.70	116
				Beaver Lodge (N. Dak.)	0.20	116
				Texas	0.41	116
				Alida (S.E. Sask., Can.)	0.43	116
				Lagunillas Quince (Venezuela)	0.071	116
				Redwater (Edmonton, Can.)	0.85	116
				Lee-Harrison (Tex.)	0.14	116
				North Smyer (Tex.)	1.32	116
				Hastings (Tex.)	0.20	116
				Wilmington (Cal.)	0.30	116
				South Houston (Tex.)	0.081	116
				Mid-Continent Comp. (U.S.A.)	0.32 ± 0.01	116
C_7H_{14}	1, *cis*-3-Dimethylcyclopentane	90.77	Cycloparaffin	Ponca City, Okla.	0.21	17
				Makhachkala, Russia	0.97–1	48
				Saudi Arabia	0.05	116
				El Dorado Comp.	0.06	116
				Kuwait	0.06	116
				Wyoming Comp.	0.06	116
				Beaver Lodge (N. Dak.)	0.11	116
				Tia Juana (Venezuela)	0.09	116
				Teas (Tex.)	0.26	116
				Winkler (Tex.)	0.18	116
				W. Kansas Comp.	0.20	116

* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_7H_{14}	1, *cis*-3-Dimethylcyclopentane	90.77	Cycloparaffin	Eola (Okla.)	0.33	116
				Beaver Lodge (N. Dak.)	0.12	116
				Texas	0.24	116
				Alida (S.E. Sask., Can.)	0.23	116
				Lagunillas Quince (Venezuela)	0.042	116
				Redwater (Edmonton, Can.)	0.45	116
				Lee-Harrison (Tex.)	0.10	116
				North Smyer (Tex.)	0.85	116
				Hastings (Tex.)	0.12	116
				Wilmington (Cal.)	0.188	116
				South Houston (Tex.)	0.056	116
				Mid-Continent Comp. (U.S.A.)	0.183 ± 0.001	116
C_7H_{14}	1, *trans*-3-Dimethylcyclopentane	91.72	Cycloparaffin	Ponca City, Okla.	0.87	18, 9, 17
				Makhachkala, Russia	—	48
				Saudi Arabia	0.05	116
				El Dorado Comp.	0.09	116
				Kuwait	0.05	116
				Wyoming Comp.	0.07	116
				Beaver Lodge (N. Dak.)	0.10	116
				Tia Juana (Venezuela)	0.12	116
				Teas (Tex.)	0.24	116
				Winkler (Tex.)	0.18	116
				W. Kansas Comp.	0.13	116
				Eola (Okla.)	0.32	116
				Beaver Lodge (N. Dak.)	0.11	116
				Texas	0.20	116

C_7H_{14}	1, *trans*-3-Dimethylcyclopentane	91.72	Cycloparaffin	Alida (S.E. Sask., Can.)	0.19	116
				Lagunillas Quince (Venezuela)	0.039	116
				Redwater (Edmonton, Can.)	0.39	116
				Lee-Harrison (Tex.)	0.08	116
				North Smyer (Tex.)	0.73	116
				Hastings (Tex.)	0.12	116
				Wilmington (Cal.)	0.172	116
				South Houston (Tex.)	0.049	116
				Mid-Continent Comp. (U.S.A.)	0.177 ± 0.003	116
C_7H_{14}	Ethylcyclopentane	103.47	Cycloparaffin	Ponca City, Okla.	0.16	20
				Saudi Arabia	0.05	116
				El Dorado Comp.	0.05	116
				Kuwait	0.06	116
				Wyoming Comp.	0.05	116
				Beaver Lodge (N. Dak.)	0.06	116
				Tia Juana (Venezuela)	0.08	116
				Teas (Tex.)	0.14	116
				Winkler (Tex.)	0.09	116
				W. Kansas Comp.	0.10	116
				Eola (Okla.)	0.24	116
				Beaver Lodge (N. Dak.)	0.06	116
				Texas	0.16	116
				Alida (S.E. Sask., Can.)	0.11	116
				Lagunillas Quince (Venezuela)	0.024	116
				Redwater (Edmonton, Can.)	0.14	116
				Lee-Harrison (Tex.)	0.08	116
				North Smyer (Tex.)	0.17	116
				Hastings (Tex.)	0.07	116
				Wilmington (Cal.)	0.07	116

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* For Reference List see page 326.

TABDE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_7H_{14}	Ethylcyclopentane	103.47	Cycloparaffin	South Houston (Tex.)	0.04	116
				Mid-Continent Comp. (U.S.A.)	0.089 ± 0.004	116
C_7H_{14}	Methylcyclohexane	100.93	Cycloparaffin	Ponca City, Okla.	1.6	19, 9
				Makhachkala, Russia	0.68–0.74	48
				Saudi Arabia	0.37	116
				El Dorado Comp.	0.88	116
				Kuwait	0.40	116
				Wyoming Comp.	0.38	116
				Beaver Lodge (N. Dak.)	1.45	116
				Tia Juana (Venezuela)	0.64	116
				Teas (Tex.)	1.46	116
				Winkler (Tex.)	0.48	116
				W. Kansas Comp.	1.18	116
				Eola (Okla.)	0.78	116
				Beaver Lodge (N. Dak.)	1.31	116
				Texas	1.16	116
				Alida (S.E. Sask., Can.)	1.38	116
				Lagunillas Quince (Venezuela)	0.221	116
				Redwater (Edmonton, Can.)	0.93	116
				Lee-Harrison (Tex.)	0.83	116
				North Smyer (Tex.)	1.85	116
				Hastings (Tex.)	1.55	116
				Wilmington (Cal.)	0.29	116
				South Houston (Tex.)	0.78	116
				Mid-Continent Comp. (U.S.A.)	1.04 ± 0.02	116
				Yu-Men gasoline, China	—	118

C_7H_{16}	2,2,3-Trimethylbutane	80.87	Paraffin	Ponca City, Okla.	—	45
				Makhachkala, Russia	0.03 or less	48
				Zhirnovsk, Russia	—	46
				Saudi Arabia	0.003	116
				El Dorado Comp.	0.016	116
				Kuwait	0.002	116
				Wyoming Comp.	0.004	116
				Beaver Lodge (N. Dak.)	0.006	116
				Tia Juana (Venezuela)	0.004	116
				Teas (Tex.)	0.003	116
				Winkler (Tex.)	0.004	116
				W. Kansas Comp.	0.004	116
				Eola (Okla.)	0.002	116
				Beaver Lodge (N. Dak.)	0.004	116
				Texas	0.004	116
				Alida (S.E. Sask., Can.)	0.003	116
				Lagunillas Quince (Venezuela)	0.002	116
				Redwater (Edmonton, Can.)	0.002	116
				Lee-Harrison (Tex.)	0.002	116
				North Smyer (Tex.)	0.004	116
				Hastings (Tex.)	0.02	116
				Wilmington (Cal.)	0.001	116
				South Houston (Tex.)	0.007	116
				Mid-Continent Comp. (U.S.A.)	0.004 ± 0.002	116
C_7H_{16}	2,2-Dimethylpentane	79.20	Paraffin	Ponca City, Okla.	0.02	14, 9
				Makhachkala, Russia	0.18–0.24	48
				Saudi Arabia	0.009	116
				El Dorado Comp.	0.056	116
				Kuwait	0.008	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_7H_{16}	2,2-Dimethylpentane	79.20	Paraffin	Wyoming Comp.	0.012	116
				Beaver Lodge (N. Dak.)	0.031	116
				Tia Juana (Venezuela)	0.013	116
				Teas (Tex.)	0.015	116
				Winkler (Tex.)	0.014	116
				W. Kansas Comp.	0.025	116
				Eola (Okla.)	0.007	116
				Beaver Lodge (N. Dak.)	0.017	116
				Texas	0.014	116
				Alida (S.E. Sask., Can.)	0.017	116
				Lagunillas Quince (Venezuela)	0.006	116
				Redwater (Edmonton, Can.)	0.010	116
				Lee-Harrison (Tex.)	0.008	116
				North Smyer (Tex.)	0.016	116
				Hastings (Tex.)	0.038	116
				Wilmington (Cal.)	0.003	116
				South Houston (Tex.)	0.016	116
				Mid-Continent Comp. (U.S.A.)	0.014 ± 0.001	116
C_7H_{16}	3,3-Dimethylpentane	86.07	Paraffin	Ponca City, Okla.	—	45
				Makhachkala, Russia	trace	48
				Saudi Arabia	0.006	116
				El Dorado Comp.	0.038	116
				Kuwait	0.007	116
				Wyoming Comp.	0.013	116
				Beaver Lodge (N. Dak.)	0.018	116
				Tia Juana (Venezuela)	0.006	116
				Teas (Tex.)	0.008	116

C_7H_{16}	3,3-Dimethylpentane	86.07	Paraffin	Winkler (Tex.)	0.023	116
				W. Kansas Comp.	0.005	116
				Eola (Okla.)	0.004	116
				Beaver Lodge (N. Dak.)	0.010	116
				Texas	0.008	116
				Alida (S.E. Sask., Can.)	0.014	116
				Lagunillas Quince (Venezuela)	0.004	116
				Redwater (Edmonton, Can.)	0.004	116
				Lee-Harrison (Tex.)	0.005	116
				North Smyer (Tex.)	0.015	116
				Hastings (Tex.)	0.022	116
				Wilmington (Cal.)	0.002	116
				South Houston (Tex.)	0.014	116
				Mid-Continent Comp. (U.S.A.)	0.008 ± 0.001	116
C_7H_{16}	2,3-Dimethylpentane	89.78	Paraffin	Ponca City, Okla.	0.15	9, 17
				Saudi Arabia	0.14	116
				El Dorado Comp.	0.20	116
				Kuwait	0.11	116
				Wyoming Comp.	0.10	116
				Beaver Lodge (N. Dak.)	0.15	116
				Tia Juana (Venezuela)	0.10	116
				Teas (Tex.)	0.21	116
				Winkler (Tex.)	0.20	116
				W. Kansas Comp.	0.11	116
				Eola (Okla.)	0.13	116
				Beaver Lodge (N. Dak.)	0.13	116
				Texas	0.17	116
				Alida (S.E. Sask., Can.)	0.19	116
				Lagunillas Quince (Venezuela)	0.039	116

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* For Reference List see page 326.

Table 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_7H_{16}	2,3-Dimethylpentane	89.78	Paraffin	Redwater (Edmonton, Can.)	0.12	116
				Lee-Harrison (Tex.)	0.19	116
				North Smyer (Tex.)	0.32	116
				Hastings (Tex.)	0.11	116
				Wilmington (Cal.)	0.058	116
				South Houston (Tex.)	0.048	116
				Mid-Continent Comp. (U.S.A.)	0.109 ± 0.003	116
C_7H_{16}	2,4-Dimethylpentane	80.50	Paraffin	Ponca City, Okla.	0.08	9
				Makhachkala, Russia	0.18–0.24	48
				Saudi Arabia	0.039	116
				El Dorado Comp.	0.11	116
				Kuwait	0.031	116
				Wyoming Comp.	0.033	116
				Beaver Lodge (N. Dak.)	0.068	116
				Tia Juana (Venezuela)	0.037	116
				Teas (Tex.)	0.047	116
				Winkler (Tex.)	0.044	116
				W. Kansas Comp.	0.036	116
				Eola (Okla.)	0.028	116
				Beaver Lodge (N. Dak.)	0.057	116
				Texas	0.035	116
				Alida (S.E. Sask., Can.)	0.039	116
				Lagunillas Quince (Venezuela)	0.017	116
				Redwater (Edmonton, Can.)	0.030	116
				Lee-Harrison (Tex.)	0.019	116
				North Smyer (Tex.)	0.048	116
				Hastings (Tex.)	0.050	116

C_7H_{16}	2,4-Dimethylpentane	80.50	Paraffin	Wilmington (Cal.)	0.009	116
				South Houston (Tex.)	0.025	116
				Mid-Continent Comp. (U.S.A.)	0.033 ± 0.002	116
C_7H_{16}	3-Methylhexane	91.85	Paraffin	Ponca City, Okla.	0.51	9, 17, 18
				Saudi Arabia	0.55	116
				El Dorado Comp.	0.70	116
				Kuwait	0.43	116
				Wyoming Comp.	0.33	116
				Beaver Lodge (N. Dak.)	0.49	116
				Tia Juana (Venezuela)	0.34	116
				Teas (Tex.)	0.58	116
				Winkler (Tex.)	0.48	116
				W. Kansas Comp.	0.38	116
				Eola (Okla.)	0.45	116
				Beaver Lodge (N. Dak.)	0.44	116
				Texas	0.50	116
				Alida (S.E. Sask., Can.)	0.62	116
				Lagunillas Quince (Venezuela)	0.101	116
				Redwater (Edmonton, Can.)	0.38	116
				Lee-Harrison (Tex.)	0.38	116
				North Smyer (Tex.)	0.72	116
				Hastings (Tex.)	0.17	116
				Wilmington (Cal.)	0.085	116
				South Houston (Tex.)	0.080	116
				Mid-Continent Comp. (U.S.A.)	0.36 ± 0.02	116
C_7H_{16}	2-Methylhexane	90.05	Paraffin	Ponca City, Okla.	0.73	16, 9
				Makhachkala, Russia	0.44–0.5	48
				Saudi Arabia	0.43	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_7H_{16}	2-Methylhexane	90.05	Paraffin	El Dorado Comp.	0.68	116
				Kuwait	0.33	116
				Wyoming Comp.	0.27	116
				Beaver Lodge (N. Dak.)	0.47	116
				Tia Juana (Venezuela)	0.26	116
				Teas (Tex.)	0.43	116
				Winkler (Tex.)	0.27	116
				W. Kansas Comp.	0.28	116
				Eola (Okla.)	0.32	116
				Beaver Lodge (N. Dak.)	0.35	116
				Texas	0.37	116
				Alida (S.E. Sask., Can.)	0.42	116
				Lagunillas Quince (Venezuela)	0.068	116
				Redwater (Edmonton, Can.)	0.24	116
				Lee-Harrison (Tex.)	0.30	116
				North Smyer (Tex.)	0.43	116
				Hastings (Tex.)	0.15	116
				Wilmington (Cal.)	0.042	116
				South Houston (Tex.)	0.048	116
				Mid-Continent Comp. (U.S.A.)	0.28 ± 0.01	116
C_7H_{16}	*n*-Heptane	98.43	Paraffin	Ponca City, Okla.	2.3	19, 9
				Makhachkala, Russia	0.93	48
				Saudia Arabia	1.56	116
				El Dorado Comp.	1.56	116
				Kuwait	1.17	116
				Wyoming Comp.	0.68	116
				Beaver Lodge (N. Dak.)	2.32	116

C_7H_{16}	*n*-Heptane	98.43	Paraffin	Tia Juana (Venezuela)	0.73	116
				Teas (Tex.)	1.30	116
				Winkler (Tex.)	0.26	116
				W. Kansas Comp.	1.22	116
				Eola (Okla.)	1.27	116
				Beaver Lodge (N. Dak.)	1.60	116
				Texas	1.02	116
				Alida (S.E. Sask., Can.)	1.41	116
				Lagunillas Quince (Venezuela)	0.106	116
				Redwater (Edmonton, Can.)	0.86	116
				Lee-Harrison (Tex.)	0.68	116
				North Smyer (Tex.)	1.12	116
				Hastings (Tex.)	0.22	116
				Wilmington (Cal.)	0.133	116
				South Houston (Tex.)	0.078	116
				Mid-Continent Comp. (U.S.A.)	1.22 ± 0.01	116
				Yu-Men gasoline, China	—	118
C_7H_{16}	3-Ethylpentane	93.48	Paraffin	Ponca City, Okla.	0.06	17
				Makhachkala, Russia	0.06 or less	48
				Saudi Arabia	0.03	116
				El Dorado Comp.	0.05	116
				Kuwait	0.03	116
				Wyoming Comp.	0.03	116
				Beaver Lodge (N. Dak.)	0.04	116
				Tia Juana (Venezuela)	0.02	116
				Teas (Tex.)	0.04	116
				Winkler (Tex.)	0.06	116
				W. Kansas Comp.	0.04	116
				Eola (Okla.)	0.05	116

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_7H_{16}	3-Ethylpentane	93.48	Paraffin	Beaver Lodge (N. Dak.)	0.03	116
				Texas	0.04	116
				Alida (S.E. Sask., Can.)	0.05	116
				Lagunillas Quince (Venezuela)	0.008	116
				Redwater (Edmonton, Can.)	0.05	116
				Lee-Harrison (Tex.)	0.06	116
				North Smyer (Tex.)	0.10	116
				Hastings (Tex.)	0.02	116
				Wilmington (Cal.)	0.007	116
				South Houston (Tex.)	0.009	116
				Mid-Continent Comp. (U.S.A.)	0.030 ± 0.002	116
C_8H_{10}	Ethylbenzene	136.19	Aromatic	Ponca City, Okla.	0.19	30, 9
				Western Nesbit-Dag	—	47
C_8H_{10}	*p*-Xylene	138.35	Aromatic	Ponca City, Okla.	0.10	32, 9
				Western Nesbit-Dag, Russia	—	47
C_8H_{10}	*m*-Xylene	139.10	Aromatic	Ponca City, Okla.	0.51	32, 9
C_8H_{10}	*o*-Xylene	144.41	Aromatic	Ponca City, Okla.	0.27	32, 9
				Western Nesbit-Dag	—	47
C_8H_{14}	*cis*-Bicyclo-[3.3.0]-octane	136.5	Bicycloparaffin	Ponca City, Okla.	0.06	45, 109
C_8H_{14}	Bicyclo-[3.2.1]-octane	138	Bicycloparaffin	Ponca City, Okla.	0.008	45, 109
C_8H_{14}	Methylbicyclo-[2.2.1]-heptane	124.5	Bicycloparaffin	Ponca City, Okla.	0.001	45, 109
C_8H_{16}	1,1,3-Trimethylcyclopentane	104.89	Cycloparaffin	Ponca City, Okla.	0.30	20
				Saudi Arabia	0.02	116
				El Dorado Comp.	0.04	116
				Kuwait	0.02	116
				Wyoming Comp.	0.03	116

C_8H_{16}	1,1,3-Trimethylcyclopentane	104.89	Cycloparaffin	Beaver Lodge (N. Dak.)	0.06	116
				Tia Juana (Venezuela)	0.03	116
				Teas (Tex.)	0.17	116
				Winkler (Tex.)	0.14	116
				W. Kansas Comp.	0.11	116
				Eola (Okla.)	0.04	116
				Beaver Lodge (N. Dak.)	0.06	116
				Texas	0.10	116
				Alida (S.E. Sask., Can.)	0.12	116
				Lagunillas Quince (Venezuela)	0.017	116
				Redwater (Edmonton, Can.)	0.22	116
				Lee-Harrison (Tex.)	0.01	116
				North Smyer (Tex.)	0.47	116
				Hastings (Tex.)	0.06	116
				Wilmington (Cal.)	0.08	116
				South Houston (Tex.)	0.027	116
				Mid-Continent Comp. (U.S.A.)	0.111 ± 0.003	116
C_8H_{16}	1, *trans*-2, *cis*-4-Trimethylcyclopentane	109.29	Cycloparaffin	Ponca City, Okla.	0.2	21
C_8H_{16}	1, *trans*-2, *cis*-3-trimethylcyclopentane	110.2	Cycloparaffin	Ponca City, Okla.	0.26	21
C_8H_{16}	1,1,2-Trimethylcyclopentane	113.73	Cycloparaffin	Ponca City, Okla.	0.06	21
C_8H_{16}	1, *cis*-2, *trans*-4-Trimethylcyclopentane	116.73	Cycloparaffin	Ponca City, Okla.	0.01	8, 110
C_8H_{16}	1, *cis*-2, *trans*-3-Trimethylcyclopentane	117.5	Cycloparaffin	Ponca City, Okla.	0.07	8, 110
C_8H_{16}	1, *cis*-2, *cis*-4-Trimethylcyclopentane	118	Cycloparaffin	Ponca City, Okla.	—	45

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_8H_{16}	1, *trans*-4-Dimethylcyclohexane	119.35	Cycloparaffin	Ponca City, Okla.	0.25	8, 110
C_8H_{16}	1,1-Dimethylcyclohexane	119.54	Cycloparaffin	Ponca City, Okla.	0.06	8, 110
C_8H_{16}	1, *cis*-3-Dimethylcyclohexane	120.09	Cycloparaffin	Ponca City, Okla.	0.63	24, 8, 110
				Yu-Men gasoline, China	—	118
C_8H_{16}	1-Methyl-*trans*-3-ethylcyclopentane	120.8	Cycloparaffin	Ponca City, Okla.	0.12	8, 110
C_8H_{16}	1-Methyl-*trans*-2-ethylcyclopentane	121.2	Cycloparaffin	Ponca City, Okla.	0.14	8, 110
C_8H_{16}	1-Methyl-*cis*-3-ethylcyclopentane	121.4	Cycloparaffin	Ponca City, Okla.	0.12	8
C_8H_{16}	1, *cis*-2, *cis*-3-Trimethylcyclopentane	123	Cycloparaffin	Ponca City, Okla.	—	45
C_8H_{16}	1, *trans*-2-Dimethylcyclohexane	123.42	Cycloparaffin	Ponca City, Okla.	0.31	25, 8, 110
C_8H_{18}	1, *cis*-4-Dimethylcyclohexane	124.32	Cycloparaffin	Ponca City, Okla.	0.09	8, 110
C_8H_{16}	1, *trans*-3-Dimethylcyclohexane	124.45	Cycloparaffin	Ponca City, Okla.	0.07	8, 110
				Yu-Men, China	—	118
C_8H_{16}	Isopropylcyclopentane	126.42	Cycloparaffin	Ponca City, Okla.	0.01	8
C_8H_{18}	1-Methyl-*cis*-2-ethylcyclopentane	128.05	Cycloparaffin	Ponca City, Okla.	0.04	8
C_8H_{16}	1, *cis*-2-Dimethylcyclohexane	129.73	Cycloparaffin	Ponca City, Okla.	0.06	8
C_8H_{16}	*n*-Propylcyclopentane	130.95	Cycloparaffin	Ponca City, Okla.	0.06	8
C_8H_{16}	Ethylcyclohexane	131.78	Cycloparaffin	Ponca City, Okla.	0.37	27, 8
C_8H_{18}	2,2,4-Trimethylpentane	99.24	Paraffin	Ponca City, Okla.	—	45
			..	Saudi Arabia	0.00	116

C_8H_{18}	2,2,4-Trimethylpentane	99.24	Paraffin	El Dorado Comp.	0.00	116
				Kuwait	0.00	116
				Wyoming Comp.	0.00	116
				Beaver Lodge (N. Dak.)	0.00	116
				Tia Juana (Venezuela)	0.008	116
				Teas (Tex.)	0.00	116
				Winkler (Tex.)	0.008	116
				W. Kansas Comp.	0.00	116
				Eola (Okla.)	0.003	116
				Beaver Lodge (N. Dak.)	0.00	116
				Texas	0.00	116
				Alida (S.E. Sask., Can.)	0.00	116
				Lagunillas Quince (Venezuela)	0.00	116
				Redwater (Edmonton, Can.)	0.00	116
				Lee-Harrison (Tex.)	0.005	116
				North Smyer (Tex.)	0.006	116
				Hastings (Tex.)	0.007	116
				Wilmington (Cal.)	0.002	116
				South Houston (Tex.)	0.008	116
				Mid-Continent Comp. (U.S.A.)	0.005 ± 0.001	116
C_8H_{18}	2,2,3,3-Tetramethylbutane	106.47	Paraffin	Ponca City, Okla.	—	45
C_8H_{18}	2,2-Dimethylhexane	106.84	Paraffin	Ponca City, Okla.	0.01	20
				Mid-Continent	0.01	116
C_8H_{18}	2,5-Dimethylhexane	109.10	Paraffin	Ponca City, Okla.	0.06	21
C_8H_{18}	2,4-Dimethylhexane	109.43	Paraffin	Ponca City, Okla.	0.06	21
C_8H_{18}	2,2,4-Trimethylpentane	109.84	Paraffin	Ponca City, Okla.	0.004	21
				Zhirnovsk, Russia	—	46
C_8H_{18}	3,3-Dimethylhexane	111.97	Paraffin	Ponca City, Okla.	0.03	21
C_8H_{18}	2,3,4-Trimethylpentane	113.47	Paraffin	Ponca City, Okla.	0.005	21

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_8H_{18}	2,3,3-Trimethylpentane	114.76	Paraffin	Ponca City, Okla.	0.006	21
C_8H_{18}	2,3-Dimethylhexane	115.61	Paraffin	Ponca City, Okla.	0.07	21
C_8H_{18}	2-Methyl-3-ethylpentane	115.65	Paraffin	Ponca City, Okla.	0.06	21, 45
C_8H_{18}	2-Methylheptane	117.65	Paraffin	Ponca City, Okla.	0.90	8, 23, 110
C_8H_{18}	4-Methylheptane	117.71	Paraffin	Ponca City, Okla.	0.20	8, 110
C_8H_{18}	3,4-Dimethylhexane	117.72	Paraffin	Ponca City, Okla.	0.13	8, 110
C_8H_{18}	3-Methyl-3-ethylpentane	118.26	Paraffin	Ponca City, Okla.	0.02	8, 110
C_8H_{18}	3-Ethylhexane	118.53	Paraffin	Ponca City, Okla.	0.09	8, 110
C_8H_{18}	3-Methylheptane	118.92	Paraffin	Ponca City, Okla.	0.30	8, 110
C_8H_{18}	1-Methyl-1-ethylcyclopentane	121.52	Cycloparaffin	Ponca City, Okla.	0.03	8, 110
C_8H_{18}	*n*-Octane	125.66	Paraffin	Ponca City, Okla. Yu-Men gasoline, China	1.9 —	26, 8, 110 118
C_9H_{10}	Indan	177.8	Aromatic-cycloparaffin	Ponca City, Okla.	0.003	45, 2
C_9H_{12}	Isopropylbenzene	152.39	Aromatic	Ponca City, Okla. Western Nesbit-Dag, Russia	0.07 —	37, 9, 38 47
C_9H_{12}	*n*-Propylbenzene	159.22	Aromatic	Ponca City, Okla. Western Nesbit-Dag, Russia	0.09 —	8, 9, 38 47
C_9H_{12}	1-Methyl-3-ethylbenzene	161.30	Aromatic	Ponca City, Okla. Western Nesbit-Dag, Russia	0.17 —	38, 8 47
C_9H_{12}	1-Methyl-4-ethylbenzene	161.99	Aromatic	Ponca City, Okla. Western Nesbit-Dag, Russia	0.06 —	38, 8 47
C_9H_{12}	1,3,5-Trimethylbenzene	164.72	Aromatic	Ponca City, Okla. Western Nesbit-Dag, Russia	0.12 —	39, 38 47
C_9H_{12}	1-Methyl-2-ethylbenzene	165.15	Aromatic	Ponca City, Okla.	0.09	38, 8
C_9H_{12}	1,2,4-Trimethylbenzene	169.35	Aromatic	Ponca City, Okla. Western Nesbit-Dag, Russia	0.51 —	38, 39, 40 47

C_9H_{12}	1,2,3-Trimethylbenzene	176.08	Aromatic	Ponca City, Okla.	0.12	39, 40
				Western Nesbit-Dag, Russia	—	47
C_9H_{12}	1,1,*cis*-3, *trans*-4-Tetramethylcyclopentane	121.6	Cycloparaffin	Ponca City, Okla.	0.04	8, 110
C_9H_{12}	1,1,3-Trimethylcyclohexane	136.63	Cycloparaffin	Ponca City, Okla.	0.2	31
C_9H_{12}	1, *trans*-2, *trans*-4-Trimethylcyclohexane	141.22	Cycloparaffin	Ponca City, Okla.	0.2	45
C_9H_{12}	1, *trans*-2, *cis*-4-Trimethylcyclohexane	145.6	Cycloparaffin	Ponca City, Okla.	0.1	45
C_9H_{12}	1,1,3,3-Tetramethylcyclopentane	117.96	Cycloparaffin	Ponca City, Okla.	—	45
C_9H_{12}	2,2,4,4-Tetramethylpentane	122.28	Paraffin	Ponca City, Okla.	—	45
C_9H_{12}	2,2,5-Trimethylhexane	124.08	Paraffin	Ponca City, Okla.	0.002	8, 110
C_9H_{12}	2,2,4-Trimethylhexane	126.54	Paraffin	Ponca City, Okla.	—	45
C_9H_{12}	1, *trans*-2, *cis*-3, *trans*-4-Tetramethylcyclopentane	127.4	Cycloparaffin	Ponca City, Okla.	0.11	45
C_9H_{12}	1,1, *cis*-2, *trans*-3-Tetramethylcyclopentane	130	Cycloparaffin	Ponca City, Okla.	—	45
C_9H_{12}	1,1, *cis*-2, *cis*-3-Tetramethylcyclopentane	130	Cycloparaffin	Ponca City, Okla.	—	45
C_9H_{12}	1,1, *cis*-2, *trans*-4-Tetramethylcyclopentane	130	Cycloparaffin	Ponca City, Okla.	—	45
C_9H_{20}	1, *cis*-2, *trans*-3, *cis*-4-Tetramethylcyclopentane	131	Cycloparaffin	Ponca City, Okla.	—	45
C_9H_{20}	1, *trans*-2, *trans*-3, *cis*-4-Tetramethylcyclopentane	131	Cycloparaffin	Ponca City, Okla.	—	45
C_9H_{20}	2,3, 5-Trimethylhexane	131.34	Paraffin	Ponca City, Okla.	0.03	8
C_9H_{20}	2,6-Dimethylheptane	135.21	Paraffin	Ponca City, Okla.	0.05	28, 29

* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
C_9H_{20}	2,3-Dimethylheptane	140.5	Paraffin	Ponca City, Okla.	0.05	33
C_9H_{20}	4-Methyloctane	142.48	Paraffin	Ponca City, Okla.	0.1	34
C_9H_{20}	2-Methyloctane	143.26	Paraffin	Ponca City, Okla.	0.4	34
C_9H_{20}	3-Methyloctane	144.18	Paraffin	Ponca City, Okla.	0.1	34
C_9H_{20}	*n*-Nonane	150.80	Paraffin	Ponca City, Okla.	1.8	35,36, 8
				Elshansk, Russia	—	50
				Sokolovogorsk, Russia	—	50
$C_{10}H_8$	Naphthalene	217.96	Aromatic	Ponca City, Okla.	0.06	44
				Agha Jari, Iran	—	58
$C_{10}H_{12}$	1-Methylindan	190.6	Aromatic-cycloparaffin	Ponca City, Okla.	0.022	45
$C_{10}H_{12}$	2-Methylindan	191.4	Aromatic-cycloparaffin	Ponca City, Okla.	0.022	45
$C_{10}H_{12}$	4-Methylindan	205.5	Aromatic-cycloparaffin	Ponca City, Okla.	0.03	45
$C_{10}H_{12}$	1,2,3,4-Tetrahydronaphthalene	207.57	Aromatic-cycloparaffin	Ponca City, Okla.	0.03	43
$C_{10}H_{14}$	tert-Butylbenzene	169.12	Aromatic	Ponca City, Okla.	0.01	38
$C_{10}H_{14}$	Isobutylbenzene	172.76	Aromatic	Ponca City, Okla.	0.008	2, 45
$C_{10}H_{14}$	sec-Butylbenzene	173.30	Aromatic	Ponca City, Okla.	0.017	2, 45
$C_{10}H_{14}$	1-Methyl-3-isopropylbenzene	175.14	Aromatic	Ponca City, Okla.	0.08	2, 45
$C_{10}H_{14}$	1-Methyl-4-isopropylbenzene	177.10	Aromatic	Ponca City, Okla.	0.04	2, 45
$C_{10}H_{14}$	1-Methyl-2-isopropylbenzene	178.15	Aromatic	Ponca City, Okla.	0.009	2, 45
$C_{10}H_{14}$	1-Methyl-3-isopropylbenzene	183.27	Aromatic	Ponca City, Okla.	—	8

$C_{10}H_{14}$	*n*-Butylbenzene	183.27	Aromatic	Ponca City, Okla.	0.026	45
$C_{10}H_{14}$	1-Methyl-4-propylbenzene	183.30	Aromatic	Ponca City, Okla.	0.027	45
$C_{10}H_{14}$	2,2-Diethylbenzene	183.42	Aromatic	Ponca City, Okla.	0.005	45
$C_{10}H_{14}$	1,3-Dimethyl-5-ethylbenzene	183.58	Aromatic	Ponca City, Okla.	0.063	45
$C_{10}H_{14}$	1,2-Diethylbenzene	183.42	Aromatic	Ponca City, Okla.	—	8
$C_{10}H_{14}$	1,4-Diethylbenzene	183.78	Aromatic	Ponca City, Okla.	0.007	45
$C_{10}H_{14}$	1-Methyl-2-propylbenzene	184.80	Aromatic	Ponca City, Okla.	0.046	8, 45
$C_{10}H_{14}$	1,4-Dimethyl-2-ethylbenzene	186.83	Aromatic	Ponca City, Okla.	—	8
$C_{10}H_{14}$	1,3-Dimethyl-4-ethylbenzene	188.20	Aromatic	Ponca City, Okla.	0.050	8, 45
$C_{10}H_{14}$	1,2-Dimethyl-4-ethylbenzene	189.48	Aromatic	Ponca City, Okla.	0.057	45
$C_{10}H_{14}$	1,3-Dimethyl-2-ethylbenzene	190.01	Aromatic	Ponca City, Okla.	0.014	45
$C_{10}H_{14}$	1,2-Dimethyl-3-ethylbenzene	193.91	Aromatic	Ponca City, Okla.	—	8
$C_{10}H_{14}$	1,2,4,5-Tetramethylbenzene	196.80	Aromatic	Ponca City, Okla.	—	8
$C_{10}H_{14}$	1,2,3,5-Tetramethylbenzene	198.00	Aromatic	Ponca City, Okla.	—	8
$C_{10}H_{14}$	1,2,3,4-Tetramethylbenzene	205.04	Aromatic	Ponca City, Okla.	0.2	43
$C_{10}H_{16}$	Adamantane		Polycycloparaffin	Hodonin, Yugoslavia (?)	— 0.03	97, 104 107
$C_{10}H_{18}$	*trans*-Decahydronaphthalene	187.25	Bicycloparaffin	Ponca City, Okla.	—	8
$C_{10}H_{22}$	5-Methylnonane	165.1	Paraffin	Ponca City, Okla.	—	45
$C_{10}H_{22}$	4-Methylnonane	165.7	Paraffin	Ponca City, Okla.	0.1	8
$C_{10}H_{22}$	2-Methylnonane	166.8	Paraffin	Ponca City, Okla.	0.3	8

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* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
$C_{10}H_{22}$	3-Methylnonane	167.8	Paraffin	Ponca City, Okla.	0.1	8
$C_{10}H_{22}$	*n*-Decane	174.12	Paraffin	Ponca City, Okla.	1.8	41, 8
				Elshansk, Russia	—	50
				Sokolovogorsk, Russia	—	50
$C_{11}H_{10}$	2-Methylnaphthalene	241.05	Aromatic	Ponca City, Okla.	0.2	44
				Romaskin, Russia	—	49
$C_{11}H_{10}$	1-Methylnaphthalene	244.64	Aromatic	Ponca City, Okla.	0.1	44
				Romaskin, Russia	—	49
$C_{11}H_{14}$	2-Methyl-1,2,3,4-tetrahydronaphthalene	220.7	Aromatic	Ponca City, Okla.	0.04	45
$C_{11}H_{14}$	6-Methyl-1,2,3,4-tetrahydronaphthalene	229.3	Aromatic	Ponca City, Okla.	0.09	43
$C_{11}H_{14}$	5-Methyl-1,2,3,4-tetrahydronaphthalene	234.35	Aromatic	Ponca City, Okla.	0.08	43
$C_{11}H_{16}$	1-Methyl-3-*n*-butylbenzene	204.1	Aromatic	Ponca City, Okla.	0.06	45
$C_{11}H_{16}$	1,3-Dimethyl-4-*n*-propylbenzene	206.6	Aromatic	Ponca City, Okla.	0.03	8
$C_{11}H_{16}$	1,2-Dimethyl-4-*n*-propylbenzene	208.5	Aromatic	Ponca City, Okla.	0.03	8
$C_{11}H_{21}$	*n*-Undecane	195.89	Paraffin	Ponca City, Okla.	1.6	8, 42
				Elshansk, Russia	—	50
				Sokolovogorsk, Russia	—	50
$C_{12}H_{10}$	Biphenyl	255.2	Aromatic	West Edmond Field, Okla.	0.002–0.003	7
				Ponca City, Okla.	0.03	45
$C_{12}H_{12}$	1,2-Dimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{12}H_{12}$	1,6-Dimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{12}H_{12}$	2,6-Dimethylnaphthalene	262	Aromatic	Ponca City, Okla.	—	8
				Romaskin, Russia	—	49

$C_{12}H_{26}$	*n*-Dodecane	216.28	Paraffin	Ponca City, Okla.	1.4	44
				Elshansk, Russia	—	50
				Sokolovogorsk, Russia	—	50
$C_{13}H_{12}$	3-Methylbiphenyl	—	Aromatic	West Edmond Field, Okla.	0.002–0.003	7
$C_{13}H_{14}$	1,2,5-Trimethylnaphthalene	—	Aromatic	Trinidad	—	6
				Romaskin, Russia	—	49
$C_{13}H_{14}$	1,2,6-Trimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{13}H_{14}$	1,2,7-Trimethylnaphthalene	—	Aromatic	Trinidad	—	6
$C_{13}H_{14}$	1,2,8-Trimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{13}H_{14}$	1,3,5-Trimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{13}H_{14}$	1,3,7-Trimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{13}H_{14}$	1,3,8-Trimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{13}H_{14}$	1,6,7-Trimethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{13}H_{14}$	2,3,6-Trimethylnaphthalene	—	Aromatic	Trinidad	1% of 267°–278° distillate	6
				Romaskin, Russia	—	49
$C_{13}H_{28}$	*n*-Tridecane	235.43	Paraffin	Ponca City, Okla.	1.2	8
				Elshansk, Russia	—	50
				Sokolovogorsk, Russia	—	50
$C_{14}H_{16}$	1,4,5,7-Tetramethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{14}H_{16}$	2,3,6,7-Tetramethylnaphthalene	—	Aromatic	Romaskin, Russia	—	49
$C_{14}H_{30}$	*n*-Tetradecane	253.52	Paraffin	Ponca City, Okla.	1.0	8
				Sokolovogorsk, Russia	—	50
				Elshansk, Russia	—	50
$C_{15}H_{32}$	*n*-Pentadecane	270.61	Paraffin	Ponca City, Okla.	0.8	8
				Elshansk, Russia	—	50
$C_{16}H_{14}$	1,8-Dimethylphenanthrene	—	Aromatic	Kuwait	—	52
$C_{16}H_{14}$	2,6-Dimethylanthracene	—	Aromatic	Kuwait	—	54

* For Reference List see page 326.

TABLE 1—*Continued*

Formula	Name	B.p., °C.	Type	Source	% in Oil	References*
$C_{16}H_{14}$	2,7-Dimethylanthracene	—	Aromatic	Kuwait	—	54
$C_{16}H_{34}$	*n*-Hexadecane	286.79	Paraffin	Ponca City, Okla.	0.6	8
				Elshansk, Russia	—	50
$C_{17}H_{12}$	1-Methylpyrene	—	Aromatic	Kuwait	—	52
$C_{17}H_{12}$	1,2-Benzofluorene	—	Aromatic	Kuwait	—	52
$C_{17}H_{16}$	1,2,8-Trimethylphenanthrene	—	Aromatic	Kuwait	—	52
$C_{17}H_{16}$	2,3,6-Trimethylanthracene	—	Aromatic	Kuwait	—	54
$C_{17}H_{36}$	*n*-Heptadecane	302.15	Paraffin	Ponca City, Okla.	0.7	8
				Elshansk, Russia	—	50
$C_{18}H_{14}$	8-Methyl-1,2-benzofluorene	—	Aromatic	Kuwait	—	52
$C_{18}H_{18}$	1,3,6,7-Tetramethylanthracene	131–132 (m.p.)	Aromatic	Kuwait	—	54
$C_{18}H_{18}$	1,3,5,7-Tetramethylanthracene	164–165 (m.p.)	Aromatic	Kuwait	—	54
$C_{18}H_{18}$	2,3,6,7-Tetramethylanthracene	—	Aromatic	Kuwait	—	54
$C_{18}H_{38}$	*n*-Octadecane	316.71	Paraffin	Ponca City, Okla.	0.50	45, 111
$C_{19}H_{14}$	1-Methylchrysene	253 (m.p.)	Aromatic	Mid-continent petroleum	—	5
$C_{19}H_{40}$	*n*-Nonadecane	330.6	Paraffin	Ponca City, Okla.	0.43	45, 111
$C_{20}H_{12}$	Perylene	268–269 (m.p.)	Aromatic	American crude oil	—	53
				W. Beaumont, Texas	—	4
$C_{20}H_{42}$	*n*-Eicosane	343.8	Paraffin	Ponca City, Okla.	0.37	45, 111
$C_{21}H_{44}$	*n*-Heneicosane	356.5	Paraffin	Ponca City, Okla.	0.32	45, 111
$C_{22}H_{46}$	*n*-Docosane	368.6	Paraffin	Ponca City, Okla.	0.28	45, 111
$C_{23}H_{48}$	*n*-Tricosane	380.2	Paraffin	Ponca City, Okla.	0.24	45, 111
$C_{24}H_{50}$	*n*-Tetracosane	391.3	Paraffin	Ponca City, Okla.	0.22	45, 111

$C_{25}H_{52}$	*n*-Pentacosane	401.9	Paraffin	Ponca City, Okla.	0.20	45
$C_{26}H_{54}$	*n*-Hexacosane	412.2	Paraffin	Ponca City, Okla.	0.18	45
$C_{27}H_{56}$	*n*-Heptacosane	422.1	Paraffin	Ponca City, Okla.	0.16	45
$C_{28}H_{58}$	*n*-Octacosane	431.6	Paraffin	Ponca City, Okla.	0.14	45
$C_{29}H_{60}$	*n*-Nonacosane	440.8	Paraffin	Ponca City, Okla.	0.13	45
$C_{30}H_{62}$	*n*-Triacontane	449.7	Paraffin	Ponca City, Okla.	0.12	45
$C_{31}H_{64}$	*n*-Hentriacontane	458	Paraffin	Ponca City, Okla.	0.11	45
$C_{32}H_{66}$	*n*-Dotriacontane	467	Paraffin	Ponca City, Okla.	0.10	45

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* For Reference List see page 326.

TABLE 2

Sulfur-Containing Compounds Identified in Crude Oil

Formula	Name	B.p., °C.	Source	% in Oil	References*
CH_4S	Methanethiol	6.5	Wasson, Texas	0.0024	1, 70
			Naft-Khaneh, Iran		104
			Agha Jari, Iran		104
			Masjid-i-Sulaiman, Iran		105
C_2H_6S	Ethanethiol	35.04	Wasson, Texas	0.0053	1, 70
			Naft-Khaneh, Iran		104
			Agha Jari, Iran		104
			Maidan-i-Naftun, Iran		105
C_2H_6S	2-Thiapropane	37.3	Wasson, Texas	0.0088	1, 70
			Ohio		65
C_3H_8S	2-Propanethiol	52.6	Wasson, Texas	0.00199	1, 70
			Naft-Khaneh, Iran		104
			Agha Jari, Iran		3, 104
			Maidan-i-Naftun, Iran		105
			Iran		99
C_3H_8S	2-Thiabutane	66.6	Wasson, Texas	0.00222	1, 70
			Agha Jari, Iran		3
			Masjid-i-Sulaiman, Iran		104, 106
			Ohio		65
C_3H_8S	1-Propanethiol	67.82	Wasson, Texas	0.00041	1, 70
			Agha Jari, Iran		3, 104
			Naft-Khaneh, Iran		104
			Iran		99
C_4H_4S	Thiophene	84	Wilmington, California	0.000032	72
C_4H_8S	Thiacyclopentane	121.2	Wasson, Texas	0.000077	1
			Iran		99, 104

C_4H_8S	Thiacyclopentane	121.2	Mexico		66
			Panuco, Mexico		67, 68
			California		69
$C_4H_{10}S$	2-Methyl-2-propanethiol	64.22	Wasson, Texas	0.00055	1, 70
			Agha Jari, Iran		3
			Iran		99
$C_4H_{10}S$	3-Methyl-2-thiabutane	84.8	Wasson, Texas	0.00064	1, 70
			Agha Jari, Iran		3
$C_4H_{10}S$	2-Butanethiol	85.15	Wasson, Texas	0.00386	1, 70
			Agha Jari, Iran		3, 104
			Naft-Khaneh, Iran		104
			Maidan-i-Naftun, Iran		105
			Iran		99
			Russia		63, 64
$C_4H_{10}S$	2-Methyl-1-propanethiol	88.72	Wasson, Texas	0.00003	1, 70
			Agha Jari, Iran		3, 104
			Naft-Khaneh, Iran		104
			Iran		99
$C_4H_{10}S$	3-Thiapentane	92.0	Wasson, Texas	0.00075	1, 70
			Agha Jari, Iran		3
			Ohio		7, 65
$C_4H_{10}S$	2-Thiapentane	95.6	Wasson, Texas	0.00030	1, 70
			Agha Jari, Iran		3
			Iran		106
$C_4H_{10}S$	1-Butanethiol	98.58	Wasson, Texas	trace	1, 70
			Agha Jari, Iran		104
			Naft-Khaneh, Iran		104
C_5H_6S	2-Methylthiophene		Wilmington, California	0.0001	72
			South Uzbekhistan, Russia		108
C_5H_6S	3-Methylthiophene		—		71

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* For Reference List see page 326.

TABLE 2—*Continued*

Formula	Name	B.p., °C.	Source	% in Oil	References*
$C_5H_{10}S$	2-Methylthiacyclopentane	132.4	Wasson, Texas	0.0023	1
			Iran		99, 104
			Mexico		67, 68
			California		69
			Agha Jari, Iran		58
$C_5H_{10}S$	3-Methylthiacyclopentane	138.2	Wasson, Texas	0.00046	1
			Iran		99, 104
			Agha Jari, Iran		58
$C_5H_{10}S$	Thiacyclohexane	141.6	Wasson, Texas	0.00032	1
			Iran		99, 104
			Mexico		66
			Panuco, Mexico		67, 68
			California		69
			Agha Jari, Iran		58
$C_5H_{10}S$	Cyclopentanethiol		Wasson, Texas		1
$C_5H_{12}S$	2,2-Dimethyl-1-propanethiol		Wasson, Texas		1, 70
			Agha Jari, Iran		3
$C_5H_{12}S$	2-Methyl-1-butanethiol		Russia		63, 64
$C_5H_{12}S$	3-Methyl-1-butanethiol		Wasson, Texas		1, 70
			Maidan-i-Naftun, Iran		105
$C_5H_{12}S$	2-Methyl-2-butanethiol	99.0	Wasson, Texas	0.00064	1
$C_5H_{12}S$	3-Methyl-2-butanethiol		Wasson, Texas		1, 70
$C_5H_{12}S$	3,3-Dimethyl-2-thiabutane	99.0	Wasson, Texas		1, 70
$C_5H_{12}S$	2-Methyl-3-thiapentane	107.3	Wasson, Texas		1, 70
			Agha Jari, Iran		3
$C_5H_{12}S$	2-Thiahexane		Wasson, Texas	0.000077	1
$C_5H_{12}S$	3-Thiahexane	118.5	Wasson, Texas	0.00012	1, 70
			Iran		104

		118.5	Ohio		65
$C_5H_{12}S$	1-Pentanethiol		Wasson, Texas		1, 70
			Russia		63, 64
$C_5H_{12}S$	2-Pentanethiol		Wasson, Texas	0.0014	1
$C_5H_{12}S$	3-Pentanethiol		Wasson, Texas	0.00126	70
			Wasson, Texas	0.00057	1, 70
$C_6H_{12}S$	2,3-Dimethylthiacyclopentane	148	Agha Jari, Iran		58, 104
$C_6H_{12}S$	2,4-Dimethylthiacyclopentane	148	Agha Jari, Iran		58, 104
$C_6H_{12}S$	*trans*-2,5-Dimethylthiacyclopentane	58.0/44 mm.	Wasson, Texas	0.0025	1
$C_6H_{12}S$	*cis*-2,5-Dimethylthiacyclopentane	60.0/45 mm.	Wasson, Texas	0.0024	1
$C_6H_{12}S$	2-Ethylthiacyclopentane	155–159	Agha Jari, Iran		58, 104
$C_6H_{12}S$	*cis*-2-Methylcyclopentanethiol		Wasson, Texas		1
$C_6H_{12}S$	Cyclohexanethiol		Wasson, Texas	0.0012	1
			West Texas		100
$C_6H_{12}S$	2-Methylthiacyclohexane	153	Wasson, Texas	0.0029	1
			Agha Jari, Iran		58, 104
$C_6H_{12}S$	3-Methylthiacyclohexane	155–159	Wasson, Texas	0.000024	1
			Agha Jari, Iran		58, 104
			Iran		99
			Mexico		66
			Panuco, Mexico		67, 68
			California		69
$C_6H_{12}S$	4-Methylthiacyclohexane	155–159	Wasson, Texas	0.000048	1
			Agha Jari, Iran		58, 104
$C_6H_{14}S$	2-Methyl-2-pentanethiol		Wasson, Texas		1, 70
$C_6H_{14}S$	4-Methyl-2-pentanethiol		Wasson, Texas		1, 70
$C_6H_{14}S$	2-Methyl-3-pentanethiol		Wasson, Texas		1, 70
$C_6H_{14}S$	3-Methyl-3-pentanethiol		Wasson, Texas		1, 70
$C_6H_{14}S$	2-Hexanethiol		Wasson, Texas	0.0028	1
$C_6H_{14}S$	3-Hexanethiol		Wasson, Texas		1, 70

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* For Reference List see page 326.

TABLE 2—*Continued*

Formula	Name	B.p., °C.	Source	% in Oil	References*
$C_6H_{14}S$	2,2-Dimethyl-3-thiapentane		Wasson, Texas	0.000058	1
$C_6H_{14}S$	2,4-Dimethyl-3-thiapentane		Wasson, Texas	0.00053	1
			Ohio		65
$C_6H_{14}S$	2-Methyl-3-thiahexane		Wasson, Texas	0.000078	1
			Iran		104
$C_6H_{14}S$	4-Methyl-3-thiahexane		Wasson, Texas	0.0050	1
$C_6H_{14}S$	3-Thiaheptane		Wasson, Texas	0.000078	1
$C_7H_{10}S$	2,3,4-Trimethylthiophene	176	Agha Jari, Iran		58, 104
$C_7H_{12}S$	2-Thia-[3.3.0]-bicyclooctane	191	Agha Jari, Iran		104
$C_7H_{12}S$	8-Thia-[3.2.1]-bicyclooctane	195	Agha Jari, Iran		55, 58
$C_7H_{12}S$	3-Thia-[3.2.1]-bicyclooctane	196	Agha Jari, Iran		55
$C_7H_{12}S$	2-Thia-[3.2.1]-bicyclooctane	197	Agha Jari, Iran		55
$C_7H_{12}S$	6-Thia-[3.2.1]-bicyclooctane	197	Agha Jari, Iran		55
$C_7H_{12}S$	*cis*-3-Thia-[3.3.0]-bicyclooctane	198	Agha Jari, Iran		55
$C_7H_{12}S$	2-Thia-[2.2.2]-bicyclooctane	209–210 (m.p.)	Agha Jari, Iran		55
$C_7H_{14}S$	2,3,5-Trimethylthiacyclopentane	155–159	Agha Jari, Iran		58, 104
$C_7H_{14}S$	3,4-Dimethylthiacyclohexane *and/or*	164	Agha Jari, Iran		58, 104
	2,3,4-Trimethylcyclopentane	164	Agha Jari, Iran		58, 104
$C_7H_{14}S$	2,6-Dimethylthiacyclohexane *and/or*	164	Agha Jari, Iran		58, 104
	2-Ethyl-5-methylthiacyclopentane	164	Agha Jari, Iran		58, 104
$C_7H_{14}S$	3-Methyl-4-ethylthiacyclopentane	180	Agha Jari, Iran		58, 104
	and/or 3-Isopropylthiacyclopentane	180	Agha Jari, Iran		58, 104
$C_7H_{16}S$	3-Thiaoctane		Ohio		65
C_8H_6S	Thianaphthene		Santa Maria Valley, Calif.		57
$C_8H_{12}S$	2,3-Dimethyl-4-ethylthiophene	193	Agha Jari, Iran		58, 104
$C_8H_{12}S$	2,4-Dimethyl-3-ethylthiophene		Agha Jari, Iran		58
$C_8H_{12}S$	3,4-Dimethyl-2-ethylthiophene		Agha Jari, Iran		58
$C_8H_{12}S$	2,3,4,5-Tetramethylthiophene	193	Agha Jari, Iran		58, 104

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$C_8H_{14}S$	3-Methyl-2-thia-[0.3.3]-bicyclooctane	193–196	Agha Jari, Iran		104
$C_8H_{14}S$	6-Thia-[0.3.4]-bicyclononane		Agha Jari, Iran		104
$C_8H_{14}S$	4-Methyl-2-thia-[0.3.3]-bicyclononane	202	Agha Jari, Iran		104
$C_8H_{14}S$	*trans*-1-Thiahydrindane	213	Agha Jari, Iran		58
$C_8H_{14}S$	*cis*-1-Thiahydrindane	214	Agha Jari, Iran		58
$C_8H_{14}S$	9-Thia-[3.3.1]-bicyclononane	155.5–158 (m.p.)	Agha Jari, Iran		55
$C_8H_{16}S$	2,3-Dimethyl-5-ethylthiacyclopentane	180	Agha Jari, Iran		58, 104
	and/or				
	2,3,6-Trimethylthiacyclohexane	180	Agha Jari, Iran		58, 104
	and/or				
	2,4-Diethylthiacyclopentane	180	Agha Jari, Iran		58, 104
$C_8H_{16}S$	2,5-Dimethyl-3-ethylthiacyclopentane	180	Agha Jari, Iran		58, 104
	and/or				
	2,3-Diethylthiacyclopentane	180	Agha Jari, Iran		58, 104
$C_8H_{18}S$	2-Octanethiol		Wasson, Texas		1
$C_8H_{18}S$	2,6-Dimethyl-4-thiaheptane		Ohio		65
$C_8H_{18}S$	5-Thianonane		Ohio		65
$C_9H_{14}S$	2,3,4-Trimethyl-5-ethylthiophene	205–206	Agha Jari, Iran		58, 104
$C_9H_{14}S$	Thiaadamantane	320 (m.p.)	Agha Jari, Iran		98, 104
$C_9H_{16}S$	3,4-Dimethyl-2-thia-[0.3.3]-bicyclooctane	209–210	Agha Jari, Iran		104
	and/or				
	4-Ethyl-2-thia-[0.3.3]-bicyclooctane	209–210	Agha Jari, Iran		104
	and/or				
	9-Methyl-6-thia-[0.3.4]-bicyclononane	209–210	Agha Jari, Iran		104
$C_9H_{20}S$	5-Thiadecane		Ohio		65
$C_{10}H_{22}S$	6-Thiaundecane		Ohio		65
$C_{12}H_{26}S$	7-Thiatridecane		Ohio		65
$C_{14}H_{12}S$	1,8-Dimethyldibenzothiophene	152–153 (m.p.)	Kuwait		51

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* For Reference List see page 326.

TABLE 3

Nitrogen-Containing Compounds Identified in Crude Oil

Formula	Name	Source	References*
C_6H_7N	3-Methylpyridine	—	95, 96
C_7H_9N	2,3-Dimethylpyridine	—	95, 96
$C_8H_{11}N$	2,3,4-Trimethylpyridine	—	95, 96
$C_8H_{11}N$	2,3,5-Trimethylpyridine	—	95, 96
$C_8H_{11}N$	3-Methyl-5-ethylpyridine	—	94, 95, 96
$C_9H_{11}N$	5,6,7,8-Tetrahydroquinoline	—	73, 95
$C_{10}H_9N$	2-Methylquinoline	—	90, 95
$C_{10}H_{13}N$	3-Cyclopentylpyridine	California	115
$C_{10}H_{13}N$	4-Cyclopentylpyridine	California	115
$C_{10}H_{15}N$	2,3-Dimethyl-6-isopropylpyridine	—	93, 95
$C_{11}H_{11}N$	2,3-Dimethylquinoline	—	89, 95
$C_{11}H_{11}N$	2,4-Dimethylquinoline	—	98, 95
$C_{11}H_{11}N$	2,8-Dimethylquinoline	—	88, 90, 95, 126
$C_{11}H_{17}N$	dl-2-*sec*-Butyl-4,5-dimethylpyridine	—	92, 95, 127
$C_{12}H_9N$	Carbazole	Wilmington, California	56
$C_{12}H_{13}N$	2,3,8-Trimethylquinoline	—	87, 90, 95
$C_{12}H_{13}N$	2,4,8-Trimethylquinoline	—	86, 95
$C_{12}H_{13}N$	2-Methyl-8-ethylquinoline	—	85, 95
$C_{13}H_{15}N$	2,3,4,8-Tetramethylquinoline	—	82, 95
$C_{13}H_{15}N$	2,3-Dimethyl-8-ethylquinoline	—	84, 95
$C_{13}H_{15}N$	2,4-Dimethyl-8-ethylquinoline	—	83, 95
$C_{14}H_{17}N$	2,3,8-Trimethyl-4-ethylquinoline	—	78, 95
$C_{14}H_{17}N$	2,3,4-Trimethyl-8-ethylquinoline	—	79, 95
$C_{14}H_{17}N$	2,3-Dimethyl-8-*n*-propylquinoline	—	82, 95
$C_{14}H_{17}N$	2,4-Dimethyl-8-*n*-propylquinoline	—	81, 95
$C_{15}H_{13}N$	2,3-Dimethylbenzo-[h]-quinoline	—	74, 95

$C_{15}H_{13}N$	2,4-Dimethylbenzo-[h]-quinoline	—	74, 95
$C_{15}H_{19}N$	2,3,4-Trimethyl-8-*n*-propylquinoline	—	76, 95
$C_{15}H_{19}N$	2,3,4-Trimethyl-8-isopropylquinoline	—	77, 95
$C_{15}H_{19}N$	2,3-Dimethyl-4,8-diethylquinoline	—	75, 95
$C_{15}H_{19}N$	2,4-Dimethyl-8-*sec*-butylquinoline	—	80, 95
$C_{16}H_{21}N$	2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline	—	75, 95
$C_{16}H_{25}N$	2-(2,2,6-Trimethylcyclohexyl)-4,6-dimethylpyridine	—	91, 95

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* For Reference List see page 326.

TABLE 4

Oxygen-Containing Compounds Identified in Crude Oil

Formula	Name	Source	References*
CH_2O_2	Formic acid	California	62
$C_2H_4O_2$	Acetic acid	California	62
$C_3H_6O_2$	Propionic acid	California	62
$C_4H_8O_2$	Butyric acid	California	62
		Texas	61
$C_4H_8O_2$	Isobutyric acid	California	62
$C_5H_{10}O_2$	Valeric acid	California	62
		Texas	61
$C_5H_{10}O_2$	Isovaleric acid	California	62
C_6H_6O	Phenol	Texas	61
		West Texas	123
$C_6H_6O_3$	Dimethylmaleic anhydride	California	62
		Texas	61
$C_6H_8O_4$	Dimethylmaleic acid	Texas	61
$C_6H_{10}O_2$	Cyclopentanecarboxylic acid	Signal Hill, Cal.	103
		Russia	59, 113
		Ploesti, Romania	113
$C_6H_{12}O_2$	2-Methylpentanoic acid	Signal Hill, Cal.	102
$C_6H_{12}O_2$	3-Methylpentanoic acid	Signal Hill, Cal.	102
		Romania	113
$C_6H_{12}O_2$	4-Methylpentanoic acid	Russia	59, 113
		Ploesti, Romania	113
$C_6H_{12}O_2$	*n*-Hexanoic acid	Signal Hill, Cal.	102
C_7H_8O	*o*-Cresol	Japan	123
		Romania	113
		Boryslav, Poland	59, 122

		West Texas	124
C_7H_8O	*m*-Cresol	Japan	123
		Romania	113
		Boryslav, Poland	59, 122
C_7H_8O	*p*-Cresol	Japan	123
		Romania	113
		Boryslav, Poland	59, 122
$C_7H_{12}O_2$	2-Methylcyclopentanecarboxylic acid	Signal Hill, Cal.	103
$C_7H_{12}O_2$	3-Methylcyclopentanecarboxylic acid	Signal Hill, Cal.	103
$C_7H_{12}O_2$	Cyclopentaneacetic acid	Signal Hill, Cal.	103
		Russia	59, 113
		Ploesti, Romania	113
$C_7H_{12}O_2$	Cyclohexanecarboxylic acid	Signal Hill, Cal.	103, 114
$C_7H_{14}O_2$	3-Ethylpentanoic acid	Russia	112
$C_7H_{14}O_2$	2-Methylhexanoic acid	Signal Hill, Cal.	102
$C_7H_{14}O_2$	3-Methylhexanoic acid	Signal Hill, Cal.	102
$C_7H_{14}O_2$	4-Methylhexanoic acid	Signal Hill, Cal	102
$C_7H_{14}O_2$	5-Methylhexanoic acid	Signal Hill, Cal.	102
		Russia	59, 113
		Russia	112
		Ploesti, Romania	113
$C_7H_{14}O_2$	*n*-Heptanoic acid	Signal Hill, Cal.	102
$C_8H_{10}O$	1,2,3-Xylenol	Japan	123
		Romania	113
$C_8H_{10}O$	1,2,4-Xylenol	Boryslav, Poland	59, 122
		West Texas	124
$C_8H_{10}O$	1,3,4-Xylenol	Japan	123
		Boryslav, Poland	59, 122
$C_8H_{10}O$	1,3,5-Xylenol	Romania	113
		Boryslav, Poland	59, 122

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* For Reference List see page 326.

TABLE 4—*Continued*

Formula	Name	Source	References
$C_8H_{10}O$	1,3,5-Xylenol	West Texas	123
$C_8H_{14}O_2$	2,2-Dimethylcyclopentanecarboxylic acid	Romania	119
$C_8H_{14}O_2$	3-Methylcyclopentylacetic acid	Signal Hill, Cal.	103
		Russia	59, 113
$C_8H_{14}O_2$	4-Methylcyclohexanecarboxylic acid	Texas	61, 114
$C_8H_{16}O_2$	2,3-Dimethylcyclopentylacetic acid	Signal Hill, Cal.	114
$C_8H_{16}O_2$	*n*-Octanoic acid	Signal Hill, Cal.	102
		Texas	61
$C_9H_{16}O_2$	1,1,2-Trimethylcyclopentanecarboxylic acid	Signal Hill, Cal.	114
$C_9H_{16}O_2$	2,3-Dimethylcyclopentylacetic acid	Signal Hill, Cal.	103
$C_9H_{16}O_2$	2-Methylcyclopentylpropionic acid	Romania	119
$C_9H_{18}O_2$	*n*-Nonanoic acid	Signal Hill, Cal.	102
$C_{10}H_8O$	β-Naphthol	Boryslav, Poland	122, 128
$C_{10}H_{16}O_4$	1,2,2-Trimethylcyclopentane-1,3-dicarboxylic acid	California	62
$C_{10}H_{18}O_2$	3,3,4-Trimethylcyclopentylacetic acid	Romania	119
		California	119
$C_{10}H_{18}O_2$	*cis*-2,2,6-Trimethylcyclohexanecarboxylic acid	Signal Hill, Cal.	103, 114
$C_{10}H_{18}O_2$	*trans*-2,2,6-Trimethylcyclohexanecarboxylic acid	California	60, 114
$C_{14}H_{28}O_2$	Myristic acid	Japan	120
		Boryslav, Poland	59, 122
$C_{16}H_{32}O_2$	Palmitic acid	Japan	120
		California	121
		Borneo	121
		Boryslav, Poland	59, 122
$C_{18}H_{36}O_2$	Stearic acid	Japan	120
		Boryslav, Poland	59, 122
$C_{20}H_{40}O_2$	Arachidic acid	Japan	120
		Boryslav, Poland	59, 122

* For Reference List see page 326.

The development in recent years of fields yielding sour gas and sulfur-bearing crude oil has enhanced interest in the nature of the sulfur-bearing compounds that occur in such petroleums. Here again, early work was supported by the American Petroleum Institute, this time at the University of Texas; more recent studies have been carried out by the U.S. Bureau of Mines and in England, the latter work being carried out on Iranian oil.

As shown in Table 2, about 90 sulfur-containing compounds have been identified in crude oils. These compounds include thiols, heterocyclic derivatives such as those of thiophene, bicyclo and polycyclo compounds, and sulfides.

Nitrogen compounds, 33 of which are shown in Table 3, have also been investigated intensively. These compounds, with the exception of carbazole, are derivatives of pyridine and quinoline. It is particularly noteworthy that no aliphatic amines have been identified in crude oil in spite of the fact that such compounds are not uncommon biological degradation products. It must be concluded, therefore, that any such compounds initially associated with the oil may have been cyclized.

Oxygenated compounds have long been known to occur in crude oil, and their structures have been examined in great detail. Table 4 lists 50 such compounds ranging from simple aliphatic acids, containing from 1 to 20 carbon atoms, to cyclic naphthenic acids and aromatic acids, such as phenol and β-naphthol. The tremendous diversity of these acids as to type, and especially of the naphthenic structures, is particularly worthy of note. The compounds have excited much interest for many years, and only recently have again been cited for their potential importance as agents for the differentiation and redistribution of naturally occurring hydrocarbons.

Table 5 lists a few partially identified oxygen- and sulfur-containing compounds isolated from crude oil.

Besides the nearly 400 compounds of Tables 1–5, there have also been identified in petroleum a rather large and varied number of free porphyrins and of porphyrins complexed with vanadium and nickel (see Chapter 9). Recently an ester, dioctylphthalate was isolated from crude petroleum from Utah (Phillips and Breger, 1958); this same compound has since been identified in crude oil from Colorado (Pierce *et al.*, 1958) and, by means of infrared analysis, has been noted in a petroleum from Italy (U. Colombo, personal communication). As far as can be ascertained, this is the only ester that has been identified in crude oil. Related to dioctylphthalate is phthalic acid, which has been identified in crude oils by its reaction with phenol to yield phenolphthalein (M. Louis, personal communication).

It is interesting that the compounds of Tables 1–5 are solely oxygen-, nitrogen-, or sulfur-bearing; no individual compounds have been reported as having been isolated from petroleum that contain any two of the elements. The porphyrins, if considered among the compounds in question are, of course, exceptions inasmuch as they do contain oxygen and nitrogen.

TABLE 5
Partially Identified Oxygen- and Sulfur-Containing Compounds in Crude Oil

Formula	Name	Source	References*
$C_9H_{16}O_2$	Dimethylcyclopentylacetic acid	Romania	119
$C_{10}H_{14}O$	Diethylphenol	—	123
$C_{12}H_{18}O$	Triethylphenol	—	123
$C_8H_{14}S$	Methyl-8-thia-[3.2.1]-bicyclooctane	Agha Jari, Iran	55
$C_8H_{16}S$	Butylthiophane	Iran	106
$C_9H_{18}S$	Pentylthiophane	Iran	106
$C_{10}H_{20}S$	Hexylthiophane	Canada	125
$C_{11}H_{22}S$	Heptylthiophane	Canada	125
$C_{12}H_{24}S$	Octylthiophane	Canada	125
$C_{12}H_{24}S$	Isooctylthiophane	Canada	125
$C_{13}H_{26}S$	Nonylthiophane	Canada	125
$C_{14}H_{28}S$	Decylthiophane	Canada	125
$C_{15}H_{30}S$	Undecylthiophane	Canada	125
$C_{18}H_{36}S$	Tetradecylthiophane	Canada	125
$C_{20}H_{40}S$	Hexadecylthiophane	Canada	125
$C_{22}H_{44}S$	Octadecylthiophane	Canada	125

* For Reference List see page 326.

Metallic Trace Elements

During the last fifty years, many investigations were made of the metals in asphaltic substances and in solid residues derived from crude oils. Southwick (1951), in his review of this early work noted that Hewett (1909) described samples of organic deposits containing vanadium in 1894 and is credited with the discovery of this metal in substances believed to be derived from petroleum. On the other hand, Fester (1940) has presented evidence that Antonio Raimondi noted vanadium in the asphaltic deposits of Llacsococha, Peru in 1883. Active interest in this work dates from Hewett's report and led, in the beginning of this century, to many studies of vanadium in organisms. A most noteworthy contribution was made by Treibs (1934, 1935, 1936) with publication of his widely quoted research on porphyrins in crude oils. The significance of his work, and of vanadium in porphyrin-bearing crude oils has recently been re-emphasized by the extensive research of Dunning and Moore (1957). This subject will be discussed further in its relation to the origin of oil (see also Chapter 9).

Quantitative work on the metallic elements in refinery residues, derived from crude oils, is of a much more recent date than that on natural asphalts. Herman (1936) found 0.2–0.7% of cobalt, nickel, tin and vanadium in coke formed on the cracking of crude oil. The white ash from an oil-burning steamer contained approximately 0.15% molybdenum, 0.5% nickel, and 2.5% vanadium. Thomas (1938) gives data of a similar nature. Wells (1946) analyzed petroleum coke ashes from 24 different sources and found the chief metallic constituents to be silicon, iron, aluminum, calcium, magnesium, and sodium, with occasional presence of vanadium. These materials may have been contaminants from the refinery or from boilers and flues.

Analyses of the metallic constituents by direct ashing of crude oils or volatilization in the carbon arc were made by Southwick (1951) and Bonham (1956). The latter notes that Shirey (1931) observed that vanadium and nickel concentrations are associated with asphalt-base crude oils. Prompted by this discovery, Bonham studied the relationships between asphaltenes and these metals in 5 Pennsylvanian crudes from Oklahoma. The oil with highest asphaltene content carried the greatest quantity of vanadium and nickel. The primary purpose of his study was to investigate applications of the trace-metal content of crude oils for geological purposes, recognizing oils from different basins or provinces, correlating oils from pools, and establishing environmental conditions of genesis and migration. Crude oils from 6 provinces were studied; 57 of the 66 samples were from Oklahoma. The Seminole area was contoured on maps for vanadium and nickel in the crude oils of the various pools. Bonham concluded the results to indicate that distribution of the metals is closely related to paleogeographic trends, and that the greatest concentrations of the trace metals are along ancient shorelines and that they decrease basinward.

Southwick (1951) reviewed the spectrographic work on ash from crude oil carried out by Heide (1938) and Katchenkov (1948, 1949). Nickel, copper, chromium and thallium were most commonly found, with tin, lead, molybdenum, and cobalt occurring less frequently. No silver, gold, arsenic, cadmium or zinc was detected. Skinner found crude oil from Santa Maria, California to contain 0.022% vanadium present as a porphyrin complex.

The research done by Southwick evaluated chiefly losses of metals, especially of nickel and chromium, in the ashing of crude oils, and efforts to develop a strictly quantitative method for the determination of these elements in crude oils failed. The errors and limitations of direct arcing were also discussed by him in detail.

Evidence supports the belief of Southwick that chromium is present in many crude oils in hitherto unsuspected quantities, the amounts being comparable to those of nickel, and that it is present in inorganic form.

Complete qualitative analyses were made by Southwick on combustion residues of 3 asphaltic oils and on one non-asphaltic oil. Aluminum, calcium, chromium, copper, iron, magnesium, nickel, silicon, silver, sodium, and zinc are common to all 4. Additional elements in the three asphaltic crudes are lead, manganese, rubidium, strontium, tin, and vanadium.

Southwick cites the determination by Longobardi (1947) of uranium in the ash of a San Rafael, Argentina, crude oil, and by Bogoyavlenskii (1929) of radium in ash from oils in two localities in Russia. Bell *et al.* (1940) and Tiratsoo (1941) made measurements, by counting methods, of radium and radon in crude oils and showed the radon to be in excess of quantities in equilibrium with the radium. No determinations of uranium were made.

In a later summary, Nelson (1958) listed analyses for vanadium, nickel, iron, copper and sodium in 34 California petroleums, 37 from Texas and Louisiana, 27 from the Midcontinent and Rocky Mountain areas, and 18 from foreign oil fields. The relation of vanadium content to density of the crude oils, given for 6 samples, ranges from 350 ppm V for Bachequero, Venezuela crude (13° A.P.I.), to 2.4 ppm V for San Joaquin, Venezuela oil (41° A.P.I.). More recently Nelson (1959) reported the vanadium, nickel, iron, copper, sodium, and chromium contents for 41 Venezuelan petroleums. Highest vanadium content, 1200 ppm was found in Boscan crude oil (10.1° A.P.I.).

Of great geochemical interest, and to be discussed further in succeeding sections of this chapter, is a timely paper by Baker and Hodgson (1959) on magnesium in crude oils from western Canada; the same authors have also studied the relationships of magnesium to vanadium and nickel (Hodgson 1954, Hodgson and Baker 1957, 1959).

The Reservoir

In the reservoir petroleum occupies the voids in rocks, commonly those between the grains of sand in marine sandstones. In limestones, the petroleum occurs in voids between grains of calcareous arenites, between oolites or shells, and in cavities, sometimes large. Petroleum in some terrestrial detrital beds, as in the upper Achylagl sands of Baku, Russia, and at Quiriquiri, Venezuela, is believed to have escaped from lower marine reservoirs and reached the terrestrial sands by passage along fractures. In many reservoirs, the principal voids are fractures in limestone, sandstone, or rarely even metamorphic rocks, schists, and igneous rocks.

The fluid in the voids is composed not only of petroleum but in part of saline water, usually designated interstitial water, distributed according to interfacial tensions of petroleum and salt water with the solid constituents of the reservoir. The water occupies the smaller pores and tubelike spaces where it is held by capillary forces of considerable magnitude; consequently, most reservoir rocks, especially the sands, are water wet (Parks, 1949, chapter 17).

The crude oil in the reservoir, the reservoir fluid, contains dissolved natural gas in quantities dependent on pressure, temperature, and amounts and compositions of available hydrocarbon fluids. If a deficiency of natural gas for saturation of the crude oil is present, the reservoir fluid, a liquid, may fill the reservoir. With an excess of gas, free gas rises to the upper part of the reservoir under the impermeable cover, and forms a gas cap. Under the oil zone, saline water usually fills the voids and is called bottom water. At the border of the oil field this water is edge water.

Before the reservoir is disturbed by pressure changes caused by the drilling of wells, the fluid system in its initial state is essentially in equilibrium compared to conditions during the production of oil. Shallow oil fields, being at lower pressure and temperature, differ from the deeper oil fields in the character of reservoir fluids, and at depths over about 6000 ft, dependent on the composition of the hydrocarbons, critical conditions are sometimes found in the reservoir fluid; there, condensate fields produce gaseous products containing small amounts of dissolved liquids. Natural gas fields may contain no liquid components, dry gas, or they may produce wet gas with a little natural gasoline. It is clear that the great variation in the physical and chemical characteristics of petroleum (Pirson, 1958) in the reservoirs of oil fields requires geochemical explanation.

Approach to the problem has been by consideration of differences in source materials of petroleum, of changes in petroleum in migration from sources outside of the reservoir into the reservoir, and more rarely by movements of redistribution in the reservoir. Geologic features of oil fields indicate concentration of the fluids at the reservoir site to have taken place in short periods of time in a geological sense. Therefore, changes in the composition of the reservoir fluid, maturation, is inferred in old fields over long periods of time. This process is difficult to separate from the earlier effects, especially since additions of fluid may slowly change the composition of the reservoir fluid in some reservoirs (Hubbert, 1953; Hunt, 1953). Nevertheless, the problem of the aging of oil has been attacked by a number of investigators. Barton (1934, 1937), in an early series of studies, compared the A.P.I. gravity and percentage content of fractions, over the usual range of boiling points in crude oil analyses, for Miocene, Oligocene, and Eocene Gulf Coast crude oils from depths of 3000–5000 ft, to the same characteristics of oils of corresponding age from depths of 5000–7000 ft. Changes in the oils were clearly related to depth and age of the reserviors. Progressive change was noted in the base of the oil from naphthenic to intermediate, and almost to paraffinic in the deep Eocene oils, corresponding to increasing depth and age of the reservoir. Increase in the content of the lower boiling fractions of the crude oil was found to occur with increase of depth and age.

Barton noted that the variation observed gives trenchant evidence against migration upward of deep, light crudes, or other factors related to the surface. The variation is consistent with alteration of a heavy crude oil into a much lighter crude under the influence of time and some factor or factors linked with depth below the surface. The theory was advocated by him that the ancestral crude oils of all the crude oils of Gulf Coast reservoirs were heavy naphthenic oils, and that transformation of the character of crude oil has taken place in proportion to depth and age.

The observed evolution of these crude oils is toward an increase of the ratio of hydrogen to carbon, and the data provide evidence against cracking as the main reaction during evolution. Barton favors the process of methylation as the most plausible reaction to explain the evolution, and refers to Pratt's paper of contemporaneous date.

Pratt (1934) recognized the increase of the hydrogen–carbon ratio during the evolution of petroleum deposits in their natural habitat. In its final effect at least, the process is like the commercial process of hydrogenation. He suggested the source of hydrogen to be the methane commonly found with liquid petroleum.

In measurements of the radioactive constituents in petroleum, Bell, Goodman and Whitehead (1940) found the radon content of seven Texas and Oklahoma crude oils to range from 0.47 to 0.05 × 10^{-12} c/g, and to average 10 times the amount of radon in equilibrium with the radium present. The radioactivity in the crude oils examined is quantitatively sufficient to cause appreciable chemical effects on the hydrocarbons of petroleum by α-particle irradiation during geologic time. Such reactions produce considerable quantities of hydrogen (Whitehead, 1954), especially from heavy asphaltic substances, and this hydrogen would be available for the evolutionary processes of petroleum deduced by Barton and by Pratt.

Objections to alpha radiation as a cause of chemical reactions in the generation of petroleum were raised by Brooks (1931, 1948), mainly because of the rarity of helium in natural gas associated with petroleum. This low quantity of helium is to be expected, however, since each α-particle, ending as an atom of helium, affects about 100,000 hydrocarbon molecules.

The few measurements on radioactivity of crude oils by Bell and associates need confirmation, especially in oil fields other than those sampled;

the radon in natural gas, not determined by them, should also be combined with that in crude oil to enable calculation of the radon content of the reservoir fluid.

Further research on the significance of radiation chemistry in the evolution of crude oil in the reservoir remains of geochemical interest inasmuch as the oil has been in the reservoir much longer than the time required for its original generation and its migration to the reservoir. During this period, at the reservoir site, radon in the reservoir fluid certainly was effective in producing some hydrogen.

Metallic catalysts, notably nickel and vanadium oxides, for reactions of hydrocarbons in the evolution of petroleum were mentioned by Pratt, and Southwick has called attention to the catalytic activity of chromium, proposing that chromium is a more likely catalyst than either vanadium or nickel.

Surface active catalysts were investigated by Brooks (1948), who determined the polymerizing effect of Oklahoma and other sedimentary rocks, and some minerals, on turpentine as shown below:

Mineral	% Polymer
Fuller's earth, Georgia	75
Sylvan shale	76
Red-bed clay	65
Tertiary clay	68
Greensand, New Jersey	72
Greensand, Texas	70
Gray Persian sandstone	56
Stanley Shale	57
Reagan Sandstone	50
Calvin Sandstone	46
Simpson Sandstone	34
Permian sandstone	30
Bentonite	34
Bauxite, Georgia	58
Kaolin	12

These results, with some others not included, and with those from additional experiments (Gayer, 1933) with fuller's earth, synthetic substances, and alumina on silica show, according to Brooks, that paraffins are formed from olefins, and that isomerization and splitting of the hydrocarbon molecules takes place rapidly at temperatures well below cracking temperatures. The products portray, it is reported, the same so-called "hydrocarbon dispersion" that is found in typical petroleum.

The action of fuller's earth and other surface active catalysts, Brooks has concluded, proves that many changes to be considered in accounting for the complexity of petroleums take place in presence of these catalysts at temperatures at which, in the absence of catalysts, the hydrocarbons are relatively stable. Taking note of Barton's work, he has proposed that surface active minerals, such as clays, may have been a factor in producing the changes in oil with age and depth in the Gulf Coast sand reservoirs. Furthermore, in a limestone reservoir, petroleum should undergo little or no change, inasmuch as the surface active catalysts are rare or absent.

Geologists have seriously considered Brooks' opinions and quoted him on many occasions in their studies of the variations of petroleum in reservoirs. On the whole, their conclusions have not been favorable to Brooks' proposals, but their criticism has usually not been based upon experimental work. With modern methods in clay mineralogy and improved knowledge of surface phenomena, however, further studies to test Brooks' ideas offer an attractive field for research. One point that must be remembered, however, is that in an oil-field reservoir a more complex system than solid clay-like substances and liquid hydrocarbons exists, inasmuch as the clays are wet with saline water.

In a careful and comprehensive investigation by Hunt (1953), analyses of crude oils from 180 pools in Wyoming and were related to stratigraphic factors. On the basis of detailed stratigraphic characteristics, it was concluded that the data support neither Brooks' theory nor Barton's conclusion. There is some evidence that a correlation, not found on the Gulf Coast, exists between the compositions of the Wyoming oils and their proximity to the surface, possibly because of the loss of light ends by seepage.

In Wyoming there are a great many oil seeps, and an important factor in seepage is the nature of the cap rock of the reservoir.

Conclusions by Hunt are that in Wyoming several correlations exist between crude oil composition and stratigraphy; (1) correlation between more naphthenic and aromatic (hydrogen deficient) oils with more saline conditions where chemical sediments, carbonates and sulphates were deposited; (2) more aromatic and naphthenic crude oils occur in near-shore basins within reservoirs of clastic sediments associated with sediments of higher sand-shale ratios, and (3) in Tensleep (Pennsylvanian) reservoirs crude oils correlate in composition with depth of burial. From these results, Hunt concluded that major differences between the oils are due chiefly to differences in source material and environment of deposition, depth of burial being a factor of secondary importance.

In their discussion of the significance of variations in magnesium, vanadium and nickel in crude oils of western Canada, Baker and Hodgson (1959) gave not only the content of these metallic elements in Cretaceous (13 oils), Jurassic (5), Mississippian (3), and Devonian (13) crude oils, but also the ratios of magnesium to vanadium and to nickel. All of these trace metals are lost with age, as the crude oil matures in the reservoir, but graphic plotting showed clearly that magnesium is lost at a lower rate in the reservoir than vanadium or nickel. It is apparent from such data that, though magnesium is less abundant than vanadium and nickel in reservoir fluids, it is more resistant to maturation processes under field reservoir conditions over geologic periods of time. This research of Hodgson and Baker has set a new milestone on the road to full understanding of the significance of trace metals in the evolution of petroleum in the reservoir.

Migration

The physical processes of migration of fluids in porous media are well known. The fluid in sediments is mainly water, often saline in marine sediments, and included within it are lesser amounts of petroleum and gas. Weller (1959) reviewed the process of compaction in detrital sediments in relation to the depth of burial, and refers to Hedberg (1926, 1936), who made studies of the gravitational compaction of clay and shale in wells in the oil fields of the Mid-continent and of Venezuela. The interstitial fluids are squeezed out of mud, clay and shale until the sedimentary grains and colloidal particles come into contact with each other. In sand and sandstone far less compaction is possible since colloidal effects are almost negligible and interstitial porosity is lower. The bridging of grains maintains the porosity and permeability of the sand rocks, both siliceous and calcareous arenites.

Weller has noted that the compaction of limestones is not understood. The initial porosity of most calcareous sediments is greater than that of sand, but most limestones show little evidence of compaction. Their consolidation, when it occurs, appears to have been accomplished at an early stage by the deposition of intergranular cement.

Permeable beds, or less commonly, faulted zones, provide channels for the movement of the fluids during and after compaction. Hubbert (1953) noted that migration of oil and gas occurs through a normally water-saturated environment. If the water is at rest, the environmental fluid equilibrium is one of complete hydrostatics, and the oil and gas accumulate at the highest local position to which these fluids can migrate with horizontal interface and the less dense fluid uppermost. These conditions are the familiar ones of the classical structural theory (Howell, 1934). If the water is in motion in a non-vertical direction, the impelling forces for oil and gas will not be parallel, and the 2 fluids will migrate in divergent directions. Under hydrodynamic conditions, accumulations of oil or gas invariably exhibit inclined oil-or-gas to water interfaces. Hubbert has found evidence for hydrodynamic conditions widespread in almost every oil-producing region, and his physical theories constitute a tenable basis for the geochemist to use in problems concerning migration or relocation of petroleum.

The recent discussion by Roof and Rutherford (1958) of various proposed mechanisms and rates of migration of petroleum agrees, on the whole, with the suggestions of Hubbert; there must be a mechanism that includes bodily motion of petroleum as a separate phase, or phases if free gas is present, either through stationary or with moving water. This conclusion indicates a relatively high rate of migration during the early stages of compaction, since this process, and the accompanying movements of water, decrease progressively with time. Geologists, using data on field conditions and the age of reservoir rocks of the Late Tertiary, estimate that a reservoir may be filled with the reservoir fluids found there in time of the order of magnitude of one to ten million years. Confirmation of this inference would be desirable, especially by current geochemical methods.

The direction of migration and relocation of petroleum has been determined in some oil fields. In stratigraphic-type reservoirs closed by thinning of the reservoir beds at the upper limit, such as the Glenn Pool, Oklahoma, and the East Texas Field, the entry of oil and dissolved gas along the beds is surely from the down dip, basinward direction; in both of these fields, from the west. In almost symmetrical reservoir structures, anticlinal traps, bars or reefs, no such geological criterion is available.

In recent years, geochemistry has played a successful role in the study of such reservoirs, notably in the Seminole district of Oklahoma where the oil pools are in symmetrical domes of sandstone along the crest of the Hunton Arch. For these fields, Bonham (1956) presented evidence that high content of vanadium and nickel in the crude oils, as contoured on his maps, essentially parallels the producing trend of the district and the shorelines of the Lower Pennsylvanian basin of deposition. These crude oils along the western margin are close to a shallow water, near-shore environment of Pennsylvanian time, and are near their original source. Eastward, contents of vanadium and nickel in the crude oils decrease, and at a distance of about twenty miles these two metals are no longer detectable in the oils by the methods used. Whether these eastern oils have migrated eastward and have lost a higher original content of vanadium and nickel by selective adsorption on clays or other rock constituents, or have a different source than the western crude oils and contained originally their present metallic content is not clear. Bonham concluded that regardless of the explanation chosen for the distribution of trace metals, the relationship to the paleogeographic trends appears valid and useful.

Recent research by methods in part similar to those used by Bonham, is described by Hodgson and Baker (1959) who investigated in great detail the geochemistry of 4 oil fields in western Alberta. The density (A.P.I. gravity), percentages of sulfur, asphaltenes, resin, content of vanadium and nickel, and V/Ni ratio, are given for a long list of samples of crude oils from each field. These analytical results are followed by presentation of the data with particular emphasis on the relation between character of the analysis and the locality in the field from which the oil sample was obtained.

Quoting their statements, the Lloydminster field is located in the eastern part of Alberta and the western part of Saskatchewan, and represents a major accumulation of heavy black crude oil. There are eleven small pools in small regions of clean unconsolidated sand at relatively shallow depth. The sands are of Lower Cretaceous age and shale out on all sides with a gentle regional dip southwest. Although the reserves of oil in place are major, the ultimate primary recovery of the oil will be very modest because of the low gravity and high viscosity of the oil.

The results for the analyses of 12 samples of crude oil from Lloydminster are not conclusive, but the general picture appears to be one of appreciable yet modest variation from well to well. In this respect it is not unlike the McMurray oil field (Scott *et al.* 1954). The random scattering of the results for the Lloydminster area, like those for the McMurrary area, suggests that these 2 oil pools are simply local occurrences and are not parts of an extensive over-all migration.

The Redwater oilfield is quite different from the Lloydminster field in that it produces light oil from a limestone reef of Devonian age. The oil accumulation is in the upper edge of a tilted reef lying above a water accumulation. Situated north-east of Edmonton, the reef dips southwest and is one of a chain of reefs extending southwestward.

The analytical data for the Redwater field also show appreciable, yet moderate, variations from well to well. There is a reasonably strong indication of a uniform rising trend in nickel content and associated values from northwest to southeast. The Redwater results might be interpreted on the basis of movement from the south, but the data are not clear cut because there is a general lack of agreement of the data for sulphur with the metal values.

In the Joffre area, about 100 miles south of Edmonton, oil is produced from the Viking Sand of Lower Cretaceous age, from Basal Cretaceous sands, and from the Nisku (D-2) limestone of Devonian age. At present the Viking reservoir is the principal one. Crude oils from the Joffre area showed 2 interesting features. The first was that the trend suggested by the Redwater results was apparent also in Joffre, but was much more pronounced. Where the variation in Redwater is about 50% it was nearly 100% in the Joffre Viking oils. The metal, asphaltenes, resins, and sulphur values were high along the northeastern side of the field and low along the southwestern side; the gravity was low along the northeastern side and high along the southwestern side. The second feature was that the oils from the 2 reservoirs were not identical and showed unrelated geographic patterns.

The vanadium and nickel results were similar but the asphaltenes, resin, and sulphur results were different. The Viking isoconcentration lines ran northwest and southeast, but the Nisku lines extended north and south. Production from the Viking Sand indicates movement from southwest to northeast. Nisku oils appear distinct from Viking oils in character and mode of accumulation, with a west to east movement indicated.

Pembina, the fourth major oil field in the study and probably the largest oil field in North America, is about 75 miles southwest of Edmonton. The principal production is developed in the Upper Cretaceous Cardium Sands consisting of 3 sands and a conglomerate that were laid down in cycles of advance and retreat of an Upper Cretaceous sea. Sixty-eight Cardium oil samples from Pembina were analyzed and the results indicated that the trends apparent in the other smaller fields were developed here to a very significant extent. The 50% range of variation for Redwater and the 100% range of variation for Joffre were matched in the Pembina Cardium by ten-fold variation. The Pembina Cardium oil samples were divided into 3 equal groups, described as high, medium, and low, for each set of determinations. All the results show the same pattern in the field, with a high region on the northeast edge, a low on the southwest edge, and medium between.

The Pembina Field, producing from the Cardium, extends over more than a third of a million acres. The remainder of the Cardium oil throughout Alberta is obtained from minor pools in an area of more than five million acres. Most of these minor pools were sampled and the oils analyzed. The results indicated that the oils in the minor pools were similar to the Pembina oils and showed similar variations from point to point in the fields. The most significant observation was that the northeast–southwest trend apparent within the Pembina field appeared to be extended over the entire five million acre area of scattered Cardium production.

The Pembina Cardium oil, regarded as having moved from northeast to southwest, therefore, represents a part of a vast regional design for Cardium oil fields in Alberta with general migration in that direction.

Reactions affecting petroleum during migration were proposed by Pratt (1934), Barton (1937), and Brooks (1948); their ideas regarding the effects of adsorption and other surface phenomena in the colloidal environment of the fluids during relocation on their way to the reservoir have already been discussed. The removal of some heavy fractions seems well established, but lack of experimental data in water-wet colloidal systems of clay prevents definitive statements on the effect of surface-active catalysts.

Adsorption is mentioned by Bonham (1956) in his discussion of the migration of the Seminole crude oils. Hodgson and Baker (1959) consider the general conditions surrounding the accumulation of crude oils in their Pembina study to be similar to those described by Bonham. They state that retention by the porous solids of the asphaltenes and resins, and of the vanadium, nickel, and sulfur compounds in the crude oils during migration and relocation is supported by laboratory experiments that they have made, but that are still incomplete. Further data on this subject will be welcomed by geochemists.

Metamorphism of Petroleum

Hanson (1959) noted the well-known fact that petroleum, although found in Cambrian and abundant in Ordovician strata, is not detected in Precambrian sediments, and cites studies by Rankama on the ratio of carbon-12 to carbon-13 in metamorphosed Precambrian rocks. The carbon isotope ratios determined by Nier and his associates (Murphy and Nier, 1941; Nier and Gulbranson, 1939) show little difference between coal (91.3–

92.0, average 91.8), petroleum (92.5), and bituminous shales (average 92.5). Much more study of carbon isotope ratios is needed before proof of the former existence of petroleum, even in metamorphosed Paleozoic sediments, is affirmed. Abelson (1959) casts grave doubt on petroleum formation in Precambrian time on the basis of his studies of the geochemistry of organic substances.

In a critical review of the theory of David White on progressive regional metamorphism of petroleum in relationship to that of coal, Thom (1934) accepted the theory in a broad way, but rejected it as an index always useful in exploration for oil and gas. His conclusion has been supported by Mme. Teichmüller (1958) with her detailed regional chemical and microscopic data from the petroliferous areas of the North German plain (Basse-Saxe).

Since the trend proposed during metamorphism of petroleum is towards gaseous components with a possible end product in methane, further geochemical studies of the gases in metamorphic rocks are needed to test the theory. Also of geochemical interest are the reported presence of methane in granites, and the source of the helium content of natural gas in some gas fields, usually stratigraphically near granite.

Origin of Petroleum

Geologists and chemists have long been intrigued by problems concerned with the origin of petroleum hydrocarbons. Among the earliest theories proposed was that by Berthelot, who in 1866 suggested that petroleum might be formed by the reaction of calcium carbide and water at high temperatures and pressures. A similar suggestion was later made by Mendelejeff (1877), who thought the hydrocarbons might have formed through the action of dilute acid or hot water on iron or manganese carbides. This view was supported by such great French chemists as Cloëz (1877), Moissan (1896), and Sabatier (1902). This carbide theory, based upon an inorganic origin for petroleum, is now essentially dead in view of the subsequent discoveries of optically active substances and porphyrins, both of which result from life processes, in crude oil.

The contiguous occurrence of coal and petroleum in sedimentary basins later suggested that oil was a distillation product of coal. This theory, however, attained only limited acceptance. Engler (1911–1912) took exception to coal as the progenitor and proposed, rather, that animal and vegetable debris deposited in inland seas or lagoons might have undergone bacterial degradation with removal of carbohydrates and concentration of fats and waxes. Heat and cracking led, according to Engler, to unsaturated protopetroleum, which was then converted to petroleum by contact catalysts. A number of essential features of Engler's proposal have persisted to the present.

By 1926, when the American Petroleum Institute sponsored its Research Project 1, it was recognized that most crude oils are associated with shales, and it was thought that oil could possibly be produced by the effects of pressure on the organic constituents of a shale. As a result, shearing pressure tests at room temperatures were made in steel cylinders at pressures ranging from 38,000 to more than 165,000 lb/in.^{2} on oil shales from Colorado, Kentucky, Ohio, Indiana, Australia, and Manchuria; the shales yielded by either fracture or flow, or both. In tests where shales yielded by fracture, any increased yield of bitumen by extraction after shearing was interpreted to be caused by comminution or other physical condition imposed on the sample, but in tests where the deformation under pressure took place by flowage, slight increases of yield may have been caused by chemical reactions. The conclusion was, however, that piezochemical effects on this kind of organic material are a negligible factor in the origin of petroleum (Hawley, 1929, 1930). At about this same time Stadnichenko (1929, 1931) carried out microthermal studies on 22 Eocene boghead coals and on a number of Devonian shales using a hot stage microscope. Visible changes of state, shrinkage, color changes, melting, swelling and volatilization showed that the different organic fossil constituents, spore exines, algal debris and colonies, and waxy or resinous bodies have different thermal decomposition points or ranges, distinct from those of the structureless ground mass. The temperatures required to cause visible changes were high, of the order of 200°C or higher, demonstrating the stability of the material to such temperatures.

Field and laboratory studies of the sedimentary rocks in oil fields by Trask and Patnode (1942) led to the accumulation of a vast amount of data on 8 properties of sediments:

(1) quantity of organic matter
(2) color of the sediments
(3) the reduction number, a measure of the quantity of chromic acid the sediments can reduce
(4) volatility
(5) the relative volatility, the ratio of volatility to the reduction number
(6) the ratio of carbon to nitrogen
(7) the ratio of reduction number to carbon content
(8) the nitrogen-reduction ratio, the ratio of nitrogen content to the reduction number.

The last, the nitrogen-reduction ratio was the only one of these properties that is materially different in sediments near oil zones from what it is in sediments far from oil zones, consequently, it was considered to be the best index of source beds of petroleum found during the investigation.

Trask's research, and that by Becking *et al.* on diatoms as a source of oil (1927), provided evidence that both sedimentological and biological factors are influential on a marine environment that may be a source bed for petroleum.

With recognition that both ecological and sedimentological factors enter into the formation of a potential source bed for petroleum, it was still necessary to evaluate those conditions under which oil was most likely to form and to arrive at some tentative conclusions regarding the source or sources of energy responsible for the formation of petroleum hydrocarbons from the more complex organic constituents of shales, assuming this to be the process by which petroleum is formed. Such an evaluation would necessarily be based on field observations made during the search for and recovery of crude oil if it were to be valid from a geochemical point of view. The summary and evaluation of such data was published by Cox (1946), who pointed out such pertinent facts as the organic origin of crude oil based upon the association with it of optically active compounds and porphyrins, and its low-temperature history. By means of careful consideration of many factors, Cox drew up a "geologic fence" encompassing known data that could be used as a basis for further research.

A major step forward in study of the origin of petroleum was taken in 1942 when American Petroleum Institute Research Project 43 was initiated. The stated objective of the project was to study the transformation of organic matter into petroleum, and to this end provision was made to investigate radioactive and thermal sources of energy, as well as bacteriological and biochemical factors. The objectivity of the study was demonstrated, however, by the fact that a third phase of the project was devoted to determining if petroleum-forming hydrocarbons may be formed as primary animal and vegetable products in sufficient quantity and variety to accumulate to the product called crude oil. Inasmuch as the results of these studies, which were conducted between 1945 and 1952, have in one way or another influenced much of the current thinking on the origin of petroleum, the work of A.P.I. Project 43 warrants fairly detailed discussion.

If most petroleum has formed in marine environments, as geological evidence indicates, then it is necessary to examine the environmental conditions in which marine organisms meet their ultimate fate.

The work of ZoBell and his associates during the course of A.P.I. Project 43 constitutes an impressive documentation of the functions of marine bacteria in organic sedimentation on the sea bottom, and in diagenesis of marine organic sediments. Outstanding are the papers on the redox potential of marine sediments (ZoBell, 1946), and on the microbial transformation of molecular hydrogen in these sediments (ZoBell, 1947). Of especial interest in petroleum geochemistry is the research on those marine organisms which oxidize hydrocarbons (ZoBell, 1943, 1946), and on the assimilation of hydrocarbons by microorganisms (ZoBell, 1950). Methane-oxidizing bacteria were found in marine sediments and their consumption of methane was measured (Hutton and ZoBell, 1949). It is evident that commonly in some marine environments bacteria destroy any gaseous, liquid, or solid hydrocarbons present in the bottom sediments.

ZoBell sampled the sea bottom to obtain cultures of marine bacteria, in places at great depth, and determined the effect of pressure on the bacteria in the laboratory. He also studied cores from wells in oil fields and from shallow borings on Timbalier Island in the Gulf of Mexico, Louisiana. All cores were collected with care to prevent contamination. That the samples from the shallow borings were not contaminated by material from the Earth's surface was strongly indicated by the types of bacteria which were isolated from the cores. Anaerobes predominated in most of the samples, including many which reduced sulphate and consumed hydrogen Such bacteria were found in samples to a depth of 177 ft. Living bacteria were not detected in samples from 197 to 317 ft.

Experiments were carried out (ZoBell, 1936, 1939, 1945, 1946) in which bacteria converted caproic acid to heavy hydrocarbons of the C_{20}–C_{25}. range. In other experiments, extracts from bacterial cultures contained a material indistinguishable from the ceresin waxes of crude oil. Repetitions of the experiments with certain sulphate-reducing bacteria showed that these bacteria produce small quantities of oil-like extracts from acetic, propionic, butyric, capric, palmitic, stearic and lactic acids. The small quantities produced, however, led ZoBell to conclude that these experiments did not provide an answer to the origin of oil. ZoBell, in his final report on A.P.I. Project 43A, cites later studies indicating that, besides the production of methane in abundance by many anaerobic bacteria, both liquid and solid hydrocarbons are produced as component parts of the bacterial cell substance. Assuming that only 0.1% of the cell substance is hydrocarbon, and that half of the organic content of sediments is consumed by bacteria, bacteria might convert 0.015–0.2% of the organic carbon in marine environments into hydrocarbon material. In *Serratia marinorubra*, 0.25% of the dry weight of these marine bacteria consisted of hydrocarbons. Many other marine bacteria contain on a dry basis from 0.1–1.5% liquid and solid hydrocarbon substance. Admittedly, quoting ZoBell, the amount is small, but it is of the order of magnitude that could account for the concentration of liquid and solid hydrocarbons found in recent sediments.

These facts were confirmed by Oakwood (1944–1945), who mentioned not only *Serratia marinorubra* but also the marine bacteria of species *Vibrio ponticus* that contained on a dry weight basis 0.04% hydrocarbon. In his report of the same date on the biochemical phase of this research, Stone stated that during 3 years his efforts in the bacteriological investigations had been directed toward growing large quantities of typical marine bacteria for the purpose of chemical analysis, in particular the determination of hydrocarbons using cultures isolated by ZoBell from marine mud. About 400 g of moist cells of *Serratia marinorubra* were grown, and yielded 6.5 g of extract of which 4.2 g consisted of fatty acids. A non-saponifiable red oil (0.6 g) was treated to remove alcohols, and 200 mg of colorless hydrocarbon were isolated. Since the moist cells lost 80% of their weight on drying, the hydrocarbon on a dry weight basis was 0.25%. Similar methods with *Vibrio ponticus* yielded 0.03% hydrocarbon on a dry weight basis.

Stone, at Pennsylvania State University, also conducted experiments to determine whether small amounts of hydrocarbon might be formed directly by bacterial fermentation from a known precursor. Lactic propionic, and glutamic acids, and leucine gave negative results. His conclusions were that methane-producing bacteria are widespread and abundant, that small amounts of unidentified hydrocarbons occur in the cell substance of bacteria, and that no petroleum hydrocarbon other than methane has been identified as a product of bacterial generation from a non-hydrocarbon precursor.

Oakwood also investigated the direct production of hydrocarbons by living organisms using as his principal source a large sample (500 lb) of kelp collected on the Pacific coast of California and preserved from bacterial alteration by ZoBell. The kelp was extracted and 0.03% of hydrocarbon on a dry basis was obtained. Fresh water algae were also extracted to yield 0.015% hydrocarbon.

The hydrocarbon extracts from kelp, algae, and marine bacteria were distilled, and marked positive optical rotation by hydrocarbon fractions was observed on the products from all three materials. Especial attention was given to the products obtained by extraction from the kelp. The hydrocarbon fractions derived from kelp on distillation varied in boiling points from 122° to 204°C, in molecular weight from 272 to 435, and in optical rotation from $+0.05°$ to $+0.49°$. By further concentration of the optically active components of the kelp hydrocarbons, Oakwood raised the rotatory power of fractions to $+25°$. Analysis showed these fractions to consist only of carbon and hydrogen. Further work was carried out to determine the molecular structure of the optically active hydrocarbon from the kelp and to compare it with that of the optically active material in the lubricating fractions of petroleum. Oakwood's conclusion was that the molecular structures were almost, if not exactly, identical.

That research conducted by ZoBell was designed to a great extent to determine if bacteriological processes might provide the energy necessary for the transformation of complex marine organic material into hydrocarbons. Similarly, radioactivity was investigated as an alternate source of energy. This work was based in part on the proposal by Lind (1919, 1938) and Lind and Bardwell (1926) that, if geological conditions were met where α-particle radiation affected gaseous hydrocarbons, a liquid mixture of hydrocarbons similar to petroleum might be produced. Later Bell, Goodman and Whitehead (1940) suggested that the liquid and gaseous hydrocarbons in petroleum might be formed by the effects of radiation from radioactive elements on the complex organic substances in source sediments. Results described by Sheppard (1944) confirmed the work of Lind and showed that the products of bombardment of methane with alpha particles from radon or with deuterons in a cyclotron were closely similar. Notable among the products obtained by both Lind and Sheppard were both saturated and unsaturated hydrocarbons, and large amounts of hydrogen.

After consideration of the products of bacterial decay of the organic constituents of living organisms and of the organic compounds identified in recent marine sediments, several saturated fatty acids were chosen for bombardment. The technique of the experiments, and results are given by Sheppard and Whitehead (1946). All the fatty acids bombarded, acetic, caprylic, lauric and palmitic, gave as gaseous products hydrogen, carbon dioxide, carbon monoxide and methane, and quantitative analyses were made either by standard methods of gas analysis or mass spectrometrically. The properties of the liquid products from lauric and palmitic acids indicated them to be nearly pure compounds; that from lauric acid being identified as n-undecane, and that from palmitic acid as n-pentadecane. The chemical effect of the alpha-particle radiation on these saturated fatty acids was, therefore, decarboxylation producing the hydrocarbon having one carbon atom less than the original fatty acid; dehydrogenation also occurred as indicated by the presence of hydrogen among the gaseous products. The efficiency of utilization of energy is low, and one molecule of hydrocarbon is produced by 56 eV expended by the α-particles in the substance bombarded. Although the conversion is small, calculations indicate it to be not negligible under geological conditions.

Additional radiochemical studies were carried out with fatty acids containing from 2 to 30 carbon atoms (Whitehead, Goodman, and Breger, 1951), and with cyclohexanecarboxylic acid (Breger and Burton, 1946). In all cases the acids were decarboxylated to yield corresponding hydrocarbons, both linear and cyclic. Although nuclear radiation was demonstrated to be capable of converting potential source materials into petroleum hydrocarbons, it was still necessary to evaluate the efficiency of such conversion with respect to formation of geologically significant quantities of crude oil. An attempt was made to evaluate this quantitatively by measurement of the radioactivity of probable source beds and by relating such data to the absorption of the energy by the inorganic constituents of the source beds and by the organic constituents capable of conversion to hydrocarbons, assuming such constituents to be similar to those studied in the laboratory.

On the basis of the quantitative data assembled on the yield of hydrocarbons from radiochemical reactions, on the radioactivity of probable source formations in oil fields, and on the absorption of energy, calculations were made (Whitehead, 1950–1951) of the quantity of hydrocarbons that might be produced by radiation from the uranium and thorium series and from potassium. The quantity calculated, 3×10^{-7} g of hydrocarbon per million years per gram of organic sediment, indicates that the amount of crude oil produced by radioactive processes is minute, and that it is only a minor part of the oil found in any petroleum reservoir.

The possibility that thermal energy might be important in the conversion of complex organic substances into petroleum hydrocarbons had been advanced frequently by many workers. Whitehead and Breger, in 1950, found that an organic extract from a marine mud, when heated to only 135°C, decomposed readily to yield C_4, C_5, and C_6 gaseous hydrocarbons. This study, as did that of Stadnichenko, indicated that the organic constituents of sediments may decompose by pyrolysis at relatively low temperatures. Nevertheless, the hydrocarbons formed from the mud by heating are of doubtful significance in the origin of petroleum, inasmuch as the temperature of 135°C represents, at a normal temperature gradient, a depth for oil formation of over 11,000 ft, and many oil fields were never buried to such depth. These conclusions may have to be reconsidered in view of more recent findings by Veber and Turkel'taub (1958) that gaseous hydrocarbons to and including heptanes are produced by the biochemical activity in marine mud at room temperature.

Thus in 1952, at the termination of the research on the origin of petroleum sponsored by the American Petroleum Institute, the microbiology and some aspects of the geochemistry of the organic marine source beds of petroleum had been thoroughly investigated. The processes of change in the organic constituents of organisms to petroleum by marine bacteria or by radiation chemistry were concluded to be quantitatively inadequate for the origin of the commercial amounts of crude oil in reservoirs. The identification by Oakwood of nearly identical optically active substances in marine plants and in petroleum lubricating fractions provided a link, supplementary to that of the porphyrins isolated by Triebs, between marine organic materials and petroleum, but the origin of the bulk of the petroleum in the great oil fields of the world remained unexplained.

Nevertheless, the discovery of hydrocarbon-consuming bacteria in recent marine sediments by ZoBell (1943–1946) offered a new approach, since preservation of the samples from bottom muds or in shallow drill cores is clearly necessary in order to prevent destruction of hydrocarbons by these bacteria before analysis. Immediate treatment of samples on collection by chemical preservatives, or better by freezing with Dry Ice, became an essential procedure.

Using such methods of collection of samples, Smith (1954) analyzed cores of recent sediments from several localities of the Gulf Coast, California, and the Orinoco Delta of Venezuela. Samples of recent sediment about 7 miles off Grand Isle, Louisiana, to 106 ft in depth, contained 0.026 –0.032 g of organic matter per 100 g of dried sediment. Chromatographic analysis of the organic matter yielded 6.0% paraffin-naphthene and 1.5% aromatic hydrocarbons. The age of the hydrocarbons, determined by carbon-14, was 11,800 years to 14,600 years. Algal muck and clay from the Laguna Madre flats, Texas, and from Pelican Island also yielded appreciable amounts of hydrocarbons. Hydrogen–carbon ratios varied from 1.92 to 2.01, and molecular weight from 334 to 263. The sediments from the Santa Cruz Basin, California, collected by Emery, yielded 1.9 to 2.6% paraffin-naphthenes and 3.4–16.7% aromatics, and those from the Orinoco Delta 3.9–5.7% paraffin-naphthene and 2.2–3.7% aromatics.

The quantities of hydrocarbons isolated in this work corresponded with those found by ZoBell to be products of bacterial metabolism. Nevertheless, Smith concluded that the quantities are sufficient to supply the petroleum of oil fields.

On the basis of further research on the recent organic marine sediments of Southern California, Orr and Emery (1956) agree with Smith, and state that the average potential oil yield, computed from hydrocarbons extracted from the sediments, is about ten times the eventual recovery from oil fields in the Los Angeles Basin. Later analyses of gases extracted from sediments of marshes and deep marine basins off Southern California (Emery and Hoggan, 1958) show increase of hydrocarbon gases with depth in the sediment for methane, ethane, butane, and hexane, plus isopentane, cyclobutane, cyclopentane, benzene and toluene. The high ratio of methane to ethane indicates that further diagenesis is required before these gases are like those in oil fields.

This conclusion about the hydrocarbon gases in recent sediments agrees with that of Stevens on the liquid and solid hydrocarbons in the recent marine sediments of the Gulf Coast. He states (Stevens, Bray, and Evans, 1956) that hydrocarbons in very low concentrations are a persistent constituent of the organic debris of the marine muds in the Gulf of Mexico, and of continental soils, but they differ in kind from those comprising petroleum. No oil as such was found in the upper ten feet, the maximum depth of the study, of the post-Pleistocene muds of the Gulf of Mexico. The age of the organic matter in the muds, determined by radiocarbon, ranged from 3100 to 9400 years.

In later discussion of the origin of petroleum, Stevens (1956) reaffirmed this conclusion and noted especially that the difference between hydrocarbons extracted from soils in recent sediments of marine origin and the hydrocarbons contained in crude oils and the Woodford shale resides in the relative frequency between molecules with an odd number of carbon atoms and those having an even number, in the range from docosane ($C_{22}H_{46}$) and through dotriacontane ($C_{32}H_{66}$). Mass spectrometric analyses show that the normal paraffins recovered from a number of soils and recent muds of the Gulf have a preference for an odd number of carbon atoms with nonacosane ($C_{29}H_{60}$) the most abundant member of the series. In contrast, the n-paraffin molecules from crude oil and Woodford shale are equally divided among odd and even numbers of carbon atoms. A sample of plankton also showed no odd-carbon preference. Stevens stated that the significance of these observations is not clear, but that it seems premature to conclude that the hydrocarbons in marine organisms are the sole source of petroleum hydrocarbons.

Recently, Meinschein (1959) proposed the accumulation of petroleum hydrocarbons from among the minute quantities that occur in soils and recent sediments. Recognizing certain differences between these hydrocarbons and those of petroleum, Baker (1959) suggested differential concentration by means of surface active agents capable of carrying certain hydrocarbons in aqueous suspension or in solution. In this way an attempt was made to overcome the fact that there is a preference for odd-numbered hydrocarbons in sediments that does not appear in crude oil. The suggestion that the hydrocarbons of crude oil are primary and are not derived from more complex substances is similar to that originally investigated by Oakwood and his collaborators.

In 1960 Breger suggested that the hydrocarbons of crude oil are formed from lipids, especially unsaturated lipids, by a combination of bacterial decarboxylation and the Diels–Alder reaction. It was pointed out that if this theory is correct, it can account for the formation of aliphatic, alicyclic, and aromatic hydrocarbons. No previous work has been able to account for the aromatic compounds in crude oil.

The principles of basin development, sedimentation, and the occurrence of petroleum were first outlined in reports of studies on the stratigraphy and tectonics of oil-bearing basins by Weeks (1946) and expanded in a monograph based on later research (1948). The environment determined by this analysis was called by Weeks the habitat of oil. With this title was finally published (1958) the compendious symposium under his editorship.

In this volume are 20 papers on North America, 5 on South America, 7 on Europe, 5 on the Middle East, and 4 on the Far East dealing with the types and source of oil, and the straigraphic and structural characteristics of the petroliferous basins in these regions. Typical modern basins and recent sedimentational features are discussed in papers on the basins of Southern California, Maracaibo, the Black Sea, and the Gulf of Mexico. Topical papers include a varied list of subjects, facies control of oil occurrence, oil and organic matter in source rocks of petroleum, hydrocarbons in sediments in the Gulf of Mexico, migration of oil in recent sedments in Venezuela, the chemical relationship between crude oils and their source rocks, and the dissolved hydrocarbons in subsurface waters. Last in this group are two papers on the mechanics of basin formation and evolution.

This complete and thorough description of the environmental features of the oil fields of the world contains much of interest to the geochemist. Many unsolved problems are presented that geochemical methods may aid in solution. To be noted are the source of oil in limestone fields, the high sulfur content of crude oils in limestone reservoirs, and the relationship of gas fields, condensates, normal crude oils, and petroleum of high density to the geochemical environment.

Weeks, in his introductory chapter, recognizes the place of geochemistry in any consideration of the habitat of oil. He not only reviews briefly the papers significant to the subject included in the symposium, but gives an interesting discussion of the tar belts found in some basins near the border of the sedimentary rocks, deposited in the littoral zone of the marine basin. Hedgpeth in his classification of marine environments (1957) uses commonly the term algal zone for this belt of near-shore marine sedimentation. The tar belts in Venezuela, the Middle East, and elsewhere are presently almost unexploited, with their heavy oils (9°–12° A.P.I.), but constitute a type of petroleum worth much further study from the standpoint of the relationship of varieties of petroleum to marine environments of organic sedimentation, and to the geochemistry of these environments.

Active research is taking place in petroleum geochemistry. Data from new investigations appear in publications at increasingly short intervals, and significant papers and symposia indicate an accelerating rate of development in this fertile department of geological science.

Despite the obvious incompleteness of present conclusions, unavoidable under these conditions, confident hope is expressed that attainment of conformity in genetic ideas about petroleum will come with further work on the unsolved problems, and as the results of future research are forthcoming.

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CHAPTER 8

NATIVE BITUMENS ASSOCIATED WITH OIL SHALES*

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Introduction

A VARIETY of native bitumens are present among the organic constituents of oil shales. These substances range from liquid petroleums through heavy, viscous "tars" and "asphalts" to solid asphaltites and asphaltic pyrobitumens. The deposits exist in many forms. Petroleum occupies the porous parts of adjacent strata and may even be found in pores and fractures within the oil shales. Semi-liquid "tars" and "asphalts" occur in the same manner as petroleum and in some places seep from pores or fractures of outcrops. The solid substances may occur as blebs, nodules, stringers, and veinlets in the oil shales and adjacent rocks, and as veins, some of which are of tremendous size, that cross-cut the oil shales and adjacent rocks.

The organic material that was deposited as an original constituent of oil shales generally is considered to be the source of the bitumens associated with these rocks. Until recently there has been but little investigation of the composition and chemistry of these bitumens. The following discussion is a summary of recent studies of the geology and chemistry of some of these substances found on the North American continent. The discussion is intended to be general, but because the bitumen deposits associated with the Green River Formation in the Uinta Basin of northeastern Utah have been studied in considerable detail, they are described as type examples.

Oil Shales

Oil shales occur throughout the geologic column from the Cambrian through the Tertiary systems, and undoubtedly some were deposited during the Precambrian, beginning at the time when algae and other primeval forms of life became abundant. The earliest formed oil shales have not been preserved as such, generally having been subjected to considerable metamorphism, and now appear as graphitic shales, slates, and schists. Oil shales are forming now where muds and marls rich in organic matter are being deposited under anaerobic conditions.

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* Chapter submitted in 1958.

The term "oil shale" is used loosely to designate rocks that yield liquid hydrocarbons by pyrolysis. No precise definition that adequately includes all rocks that are commonly called "oil shales" has been composed, and it is not considered practical to attempt to do so now. A small part of the organic matter present in oil shales, from 1 to 5% of the total, can be extracted with carbon disulfide, carbon tetrachloride, and other organic solvents. The bulk of the organic material is insoluble and can be made to yield hydrocarbons, or "oil", only by the application of heat. The yield of oil shales ranges from a small amount to approximately 100 gal of oil per ton of rock for some exceptionally rich material. Quite commonly a utilitarian limit is applied to the term, and rocks that yield less than about 10 gal of oil per ton are not considered to be oil shales.

Many rocks that are called "oil shales" are not shales at all. For example, most of the so-called rich "oil shale" beds of the Green River and Uinta Formations of the Uinta Basin consist predominantly of chemically precipitated carbonate minerals and are marlstones. Some of the rich beds of the Albert Shales of New Brunswick, Canada, also consist mainly of carbonate minerals. The oil shales are members of gradational rock series of which the end members are on the one hand clay shales or marlstone, and on the other are cannel coals or torbanites. They are similar in the respect that all contain significant quantities of waxy and resinous organic material.

The term "kerogen" is applied to the organic material that yields oil by pyrolysis. As discussed in Chapter 5, the nature and composition of kerogen varies from one oil shale to another; consequently, a variety of bitumens are produced from different oil shales.

Characteristics of Some Oil Shale Bitumens

The principal physical properties and some of the chemical characteristics of the most abundant oil shale bitumens are presented in Table 1. The chemical properties and compositions of these substances are discussed in a following section.

These data indicate the approximate ranges of the physical properties and ultimate compositions of the oil shale bitumens. Inasmuch as these substances are not completely uniform from one deposit to another, or even within the same deposit, minor deviations from these values are not uncommon.

Bitumen Deposits

The substances described in this paper are intimately associated with oil shales, that is, they are found within the oil shales or the adjacent rocks, and their obvious origin is from the organic matter in the oil shales. These bitumens include albertite, gilsonite, wurtzilite, some anthraxolites, some asphaltic bitumens, and other related substances. Other bitumens,

TABLE 1
Properties of Oil Shale Bitumens

	Ozocerite[1]	Tabbyite[2]	Gilsonite[3]	Wurtzilite[4]	Ingramite[5]	Albertite[6]	Anthraxolite[7]
Color	Yellow to black	Black	Black	Black	Black	Black	Black
Fracture	Conchoidal	Conchoidal	Conchoidal	Conchoidal	Conchoidal	Hackly to conchoidal	—
Lustre	Waxy	Glossy	Bright	Bright	Bright	Bright	—
Streak	White to light brown	Brown	Brown	Light brown	Brown to black	Brown to black	—
Hardness (Moh's)	1	1	2	2–3	2	2	—
Specific gravity	0.891	1.006	1.03–1.10	1.05–1.07	—	1.075–1.091	1.865
Fusing point, °F	134	178	230–350	Decomposes	Decomposes	Decomposes	—
Solubility in carbon disulphide, %	99.46	55	98	5–10	2–10	2–10	—
Solubility in petroleum naphtha, %	81.71	6.8	10–60	0–2	0.5–2	0.5–2.0	—
Mineral matter (ash), %	0.04	4.65	Trace–1	0.2–2.5	—	0.1–0.2	1.52
Fixed carbon, %	10.03	37.45	10–20	5–25	10	25–50	97.02
Carbon, %	85.35	81.32	85–86	79.5–80.0	84	83–87	94.92
Hydrogen, %	13.86	11.20	8.5–10	10.5–12.5	11.5	9–10	0.52
Sulfur, %	0.29	1.24	0.3–0.5	4.0–6.0	1.2	Trace–1.2	0.31
Nitrogen, %	0.36	2.10	2.0–2.8	1.8–2.2	1.4	0.4–3.1	1.04

[1] Bardwell and others, 1913; Ozocerite from Uinta Basin.

[2] Bardwell and others, 1913; Tabbyite from Uinta Basin.

[3] Abraham, 1945; Gilsonite from Uinta Basin.

[4] Abraham, 1945; Wurtzilite from Uinta Basin.

[5] Ingramite from Uinta Basin.

[6] Abraham, 1945; Albertite from New Brunswick, Canada.

[7] Ellis, 1897; Anthraxolite from Sudbury district, Ontario, Canada.

such as grahamite, glance pitch, and manjak, are not included because they are generally considered to be residues of inspissated petroleum, and the deposits are not associated with oil shales.

Albert County, New Brunswick, Canada—The Albert shales of Lower Carboniferous age that crop out in the southern part of New Brunswick include rich oil shale beds. These shales have been described by Bailey and Ells (1878) as follows:

"The bulk of the formation consists of shales, but while these are the prevailing rocks, there are also included, more particularly near the base and summit of the group, numerous beds of fine-grained sandstone, of greater or less thickness; and occasionally, but rarely, thin beds of conglomerate. The shales are, in general, thinly bedded, and often even papyraceous, splitting easily into thin and flexible sheets, but alternating with these are thicker and harder beds, destitute of any lamination, very tough, and breaking only with a conchoidal fracture. Both the shales and sandstones, in common with the other Lower Carboniferous rocks of the district, are highly calcareous, so much so, indeed, as sometimes to approach a true limestone in character, while both calcareous and ferruginous bands and nodules are of frequent occurrence. The most peculiar feature, however, of the group, as well as the most persistent, is the extent to which they are everywhere impregnated with bituminous matter."

The above description indicates that the Albert Shale Formation is quite similar to the lacustrine facies of the Green River and Uinta Formations of the Uinta Basin. Much of the "oil shale" of both localities is marlstone. Some of the highly kerogenous Albert Shale has a characteristic odor similar to that of the oil shales in the Uinta Formation.

Several veins of an asphaltic pyrobitumen cross-cut the shales in the vicinity of Hillsborough and Albert Mines. Many thousands of tons of this material were mined during the period from about 1850 to 1880 and used mainly in the manufacture of illuminating gas. It originally was called "albert coal" and later "albertite". The largest known vein, located about 2 miles north of Albert Mines, followed the axis of an anticline. This vein was irregular in form, was nearly vertical, averaged several feet in width, and was mined out to a depth of about 1300 ft over a distance of nearly three-quarters of a mile along the strike. Exploratory workings showed that the main vein broke up into thin stringers in a sandstone about 1500 ft below the surface. The albertite apparently does not penetrate the wall rocks, which mostly are quite impervious-appearing paper shales and calcareous shales, but does fill numerous side fractures.

The apparent source of albertite is in the organic constituents of the oil shales. Only a small part of the organic matter present in these oil shales would be required to form the solid pyrobitumen of the veins. The veins extend both above and below the apparent source beds.

Anthraxolite, Ontario, Canada—Veins of pyrobitumen occurring in the Precambrian Onwatin Slate of the Sudbury District have been described by Coleman (1897, 1928) and Mickle (1897), and similar veins occurring in the Precambrian Gunflint Formation of the Thunder Bay District have been described by Tanton (1931) and Chapman (1865). The Sudbury occurrences have been investigated quite thoroughly. The largest known vein, having a maximum width of about 9 ft, is irregular in form, nearly vertical, and cuts across the stratification of the metamorphosed slate. The original organic deposit evidently has been metamorphosed with the enclosing slates because it now has, on an ash-free basis, a high fixed carbon content, about 95%, and only about 2–5% volatile matter. Subsequent to metamorphism, the veins were fractured and considerable amounts of quartz and sulfur minerals were deposited in the openings.

In describing the Sudbury deposits Coleman (1928) states, "The conclusion was reached that the slate was originally an oil shale and that the coal-like material had reached its present position in veins cutting across the bedding of the slate as a fluid or plastic phase of petroleum." Obviously the original character of the vein material cannot be determined precisely, but the substance could have been similar to the New Brunswick albertite or to one of the pyrobitumens of the Uinta Basin.

Uinta Basin, Utah—The Uinta basin of northeastern Utah (Fig. 1) is noted for many deposits of native bitumens that occur in lacustrine and

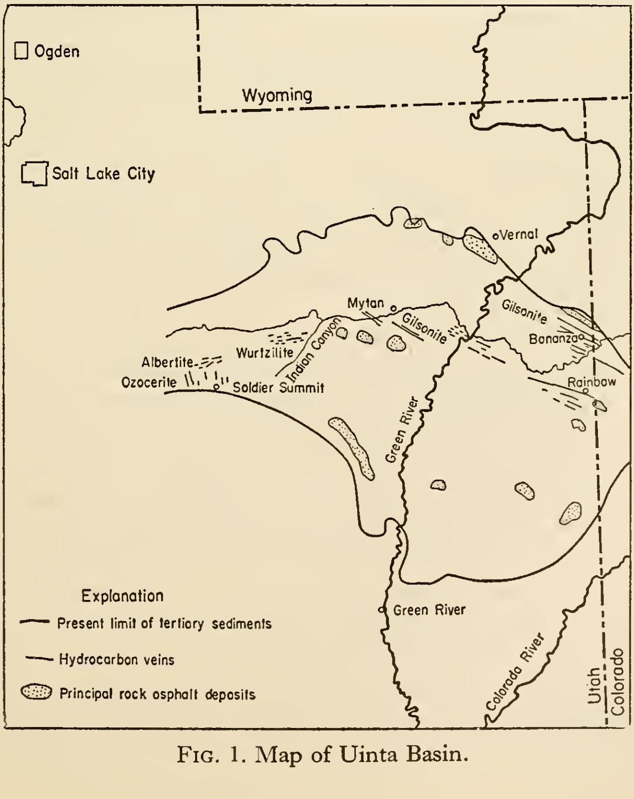

FIG. 1. Map of Uinta Basin.

fluviatile sedimentary rocks of early Tertiary age. The Uinta Basin is a structural, topographic, and sedimentary basin that was formed during the Cretaceous–Eocene transition period. During the Eocene epoch it was the site of large Lake Uinta in which was deposited a thick sequence of shales, marlstones, and limestones that includes many oil shale units. Most of the bitumens that occur within the basin are derived from these oil shales.

The Late Cretaceous and Tertiary stratigraphic section of the Uinta Basin consists of the following formations:

Tertiary:		
	Oligocene:	Duchesne River Formation—predominately alluvial sandstone and conglomerate.
	Eocene:	Uinta Formation—consists of a fluviatile sandstone facies and a lacustrine shale–marlstone–limestone facies.
		Green River Formation—includes alluvial, deltaic, and lacustrine facies.
		Wasatch Group—includes marine, fluviatile, lacustrine, and alluvial sediments, some coal beds.
Mesozoic:		
	Upper Cretaceous:	
		Mesa Verde Group—includes marine and fluviatile shales and sandstones, and a large amount of coal.
		Mancos Shale—marine shale with minor impure limestone.

During a part of the Late Cretaceous epoch the site of the Uinta Basin was a shallow seaway in which there were deposited the marine Mancos Shale and basal beds of the Mesa Verde Group. Near the close of the Late Cretaceous epoch the sea became shallower, and after some minor regressions and transgressions withdrew entirely from the area. This interval is represented by fluviatile shales and sandstones interspersed with minor marine beds of the Mesa Verde and Wasatch Groups. A thickness of several thousand feet of sediments was deposited, and these beds now crop out around the periphery of the basin.

Near the close of the Late Cretaceous epoch, or very early in the Eocene epoch, the Uinta Basin began to form, and the sedimentary environment changed to predominately lacustrine conditions. Several hundred feet of sandstones, shales, and mudstones of the middle and upper parts of the Wasatch Group were deposited around the margins of the basin while the deeper parts of the basin were cut off and started to have abnormal salinity.

Lake Uinta thus came into existence and lasted until about the beginning of the Oligocene epoch. During the life of the lake, sedimentation within the basin consisted of a lacustrine facies in the center surrounded by shore-line or deltaic facies, and locally fluviatile and alluvial facies around the edges. These facies are present in the Wasatch Group and throughout the Green River and Uinta Formations. During the early part of the Oligocene epoch the alluvial Duchesne River Formation was deposited in the northern part of the basin.

The term "Wasatch" usually has been used to designate the fluviatile and alluvial facies of the basin sediments and the term "Green River Formation" to designate the lacustrine facies. Recent usage of the terms has been to denote time–stratigraphic intervals. The deposition of lacustrine, shore-line, fluviatile, and alluvial sediments was continuous throughout the Eocene epoch although there was considerable fluctuation of the main sites of deposition and size of areas covered. The boundaries between the Wasatch–Green River and Green River–Uinta sediments are in part arbitrarily fixed.

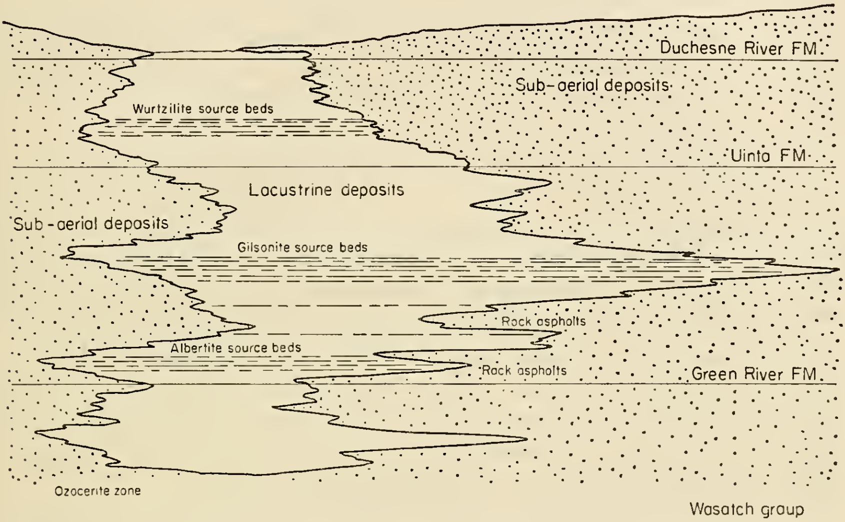

FIG. 2. Generalized section of the Uinta Basin before deformation and erosion.

A generalized section across the Uinta Basin is shown by Fig. 2. Source beds of the various kinds of bitumens are indicated within the appropriate stratigraphic intervals.

The lacustrine beds of the basin sediments are of particular interest to this discussion because they include the "oil shale" source beds of the bitumens. They consist of a sequence of interbedded paper shales and marlstones interspersed with a few sandstones, mudstones, and limestones having a total thickness of over 4000 feet. Moreover, they extend without depositional gaps from the upper part of the Wasatch Group through the entire Green River and Uinta Formations. The lacustrine beds interfinger with fluviatile sandstones and locally are overlapped by great thicknesses of them. The presence of saline minerals, predominately sulfates and carbonates, or of casts formed by crystals of these minerals, indicate that the lake waters reached a high degree of salinity. The saline constituents were mostly sulfates, carbonates, and bicarbonates and apparently included only minor quantities of chlorides. In general the salinity increased with the age of the lake. The waters, at least intermittently, were stratified, with the surface layer being aerated and supporting abundant life and the bottom layer being stagnant and sulfurous. "Oil shales" are irregularly distributed throughout the lacustrine facies. These rocks are predominately marlstones consisting of more than 50% of carbonate minerals. The beds vary from a few inches to several feet in thickness and tend to occur in groups. Some of the thickest and richest oil shale groups occur near the base of the Green River Formation in the vicinity of Soldier Summit, in the Parachute Creek Member of the middle part of the Green River Formation that extends almost throughout the entire basin, and in the Uinta Formation in the vicinity of Indian Canyon.

More complete descriptions of the stratigraphy of the Uinta basin are presented in the following references; for the Wasatch Group, Spieker and Reeside (1925), Spieker (1946); for the Green River Formation, Bradley (1931); for the Uinta Formation, Dane (1954); and for the Duchesne River Formation, Peterson and Kay (1931) and Kay (1934).

Petroleum. Petroleum occurs in stratigraphic traps in sandstones near the base of the Green River Formation at several places along the northern margin of the Uinta Basin. Crude oils recovered from the Red Wash, Roosevelt, Duchesne, County, and Flat Mesa pools are highly paraffinic with little to essentially no asphaltic constituents. Their colors range from medium green to very pale yellow, specific gravities range from 28° to 43° API, and pour points range from about 68° to 92°F because of the large amount of paraffin wax they contain. The source beds of this oil are lacustrine sediments of Wasatch and lower Green River age. Oil from a shallower Green River horizon at Duchesne is different, being asphaltic instead of paraffinic and resembling gilsonite chemically.

Shows of black, asphaltic petroleum have been found in sandstone strata of the lower and middle parts of the Green River Formation. This petroleum probably originated in oil shales or other lacustrine beds of the Green River Formation. It undoubtedly migrated from the oil shales into the fluviatile sandstones around the margin of the basin and became partially inspissated, thereby forming the rock asphalt deposits.

Ozocerite. Near Soldier Summit, at the southwest edge of the basin, the native mineral wax, ozocerite, occurs in fracture zones in soft shales and sandstones of the Wasatch Group. Within the fracture zones, which range up to about 30 ft in width, the ozocerite forms films on the brecciated rock and irregular veinlets and nodules. Reports of former mining operations indicate that ozocerite may comprise as much as 30% of the material in the fracture zones, but generally the amount is much smaller. The deposits are in Wasatch beds which are stratigraphically below the oil shales on the outcrop. The ozocerite appears to be closely related chemically to the crude oil produced at Roosevelt and Duchesne from lower horizons of the Green River facies.

Rock asphalt. Some of the largest deposits of bituminous sandstone in the United States are found along the borders of the Uinta Basin where the upturned Tertiary fluviatile sandstones are exposed or where erosion has developed deep canyons and cliff faces in them. Other deposits occur at many places within the basin, some of which are in limestone or marlstone. Most of the bitumen occurs in strata of the lower and middle parts of the Green River Formation, but locally some of it has migrated into stratigraphically lower and higher formations and even into the mantle of recent alluvium. The largest known deposits are located in the Book Cliffs near Sunnyside and P.R. Springs, in Asphalt Ridge near Vernal, and along Raven Ridge and the west side of Grand Hogback on the northeastern margin of the basin.

Infrared spectra of the organic matter extracted from sandstones in the basin are mostly similar to spectra of gilsonites, and for a few samples are similar to spectra of wurtzilites. It appears most likely that the bitumen originated in lacustrine beds of the Green River Formation, especially the oil shales. The source beds cannot be determined definitely, but they probably are in the middle or lower part of the formation below the source beds of gilsonite and above those of albertite. The bitumen has migrated laterally into permeable sands of the same age in the central and southern parts of the basin. The rock asphalts along the north side of the basin, including those at Asphalt Ridge, were formed by bitumen migrating along unconformity surfaces where the source beds are truncated by a series of post-Green River pre-Duchesne River unconformities.

Albertite. A pyrobitumen that has physical and chemical properties similar to the albertite of New Brunswick occurs in veins in lacustrine beds of the lower part of the Green River Formation near the southwest margin of the Uinta Basin. While it is unlikely that these two substances are precisely identical in composition, the resemblance is close enough that it is convenient to call the Uinta Basin material albertite also.

The Uinta Basin albertite occurs in veins within platy marlstones lying about 600 ft above the base of the Green River Formation. The veins mostly are narrow stringers from a fraction of an inch to a few inches in width and a few yards in length; but one vein (originally called nigrite by Eldridge, 1901) is at least 300 ft long, has a maximum width of about 2 ft, and has been prospected to a depth of about 30 ft. The vertical dimensions of the veins are controlled by the thicknesses of the platy marlstone strata because the veins pinch out in adjacent shaly beds. Within the veins the albertite is essentially free from wall rock fragments and other visible mineral matter. The albertite does not penetrate the wall rock but does fill small side fractures. Some of the wall rock strata contain lenses of organic matter; other strata are devoid of visually recognizable organic matter.

The source of the albertite undoubtedly is in "oil shale" beds within the platy marlstones. There is no evidence that the bitumen migrated through shaly strata separating the marlstones. The known distribution of albertite is restricted to the Soldier Summit locality.

Ingramite. Ingramite is a solid pyrobitumen occurring in lacustrine beds about 300 ft above the base of the Green River Formation in the Soldier

Summit locality. The substance is very similar to albertite and probably is a less polymerized form of it. Ingramite occurs at the stratigraphically lowest level of all the solid bitumens derived from the Uinta Basin oil shales. The beds in which it occurs crop out only in the southeastern part of the basin. The known distribution of ingramite is, therefore, restricted to this locality.

Gilsonite. The largest deposits of solid bitumen in the Uinta Basin, and possibly in the entire world, are some of the gilsonite veins. These veins are located in the northeastern part of the basin where they are spectacular features of the area because of their size and straight courses across the country. Because the size of the gilsonite veins has permitted extensive mining operations, more is known of the character of these deposits and of the association of gilsonite with its source and host rocks than of any of the other bitumens of the Uinta Basin. The gilsonite deposits, therefore, can be described in considerable detail.

Discovery of the gilsonite veins has been credited to several individuals, but these deposits must have been known to the Indians and undoubtedly were observed by the first white men who explored the area. The following statement appears in *Annual of Scientific Discovery*, 1866 and 1867 (Edited by Samuel Kneeland): "Prof. William Denton, when on an exploring trip west of the Rocky-Mountain Range, in July, 1865, found, near the junction of White and Green Rivers, a series of Tertiary beds of brown sandstone, passing occasionally into conglomerate, and thin beds of bluish and cream-colored shale alternating with the sandstones. These beds dip to the west at an angle of about 20°; and, cropping out from beneath them on the east are beds of petroleum shale, a thousand feet in thickness, varying in color from a light cream to inky blackness. One bed, ten feet in thickness, which he traced for six miles, is scarcely distinguishable from the best cannelite of New Brunswick. In the sandstone overlying the shales, he found a perpendicular vein of bitumen, resembling in lustre, fracture and other physical characters, pure albertite. This vein has a width of from two feet six inches, to three feet four inches; it lies between smooth walls of sandstone, and was traced for a distance of five miles in a nearly direct line, due west. Two more small veins were discovered parallel to the first, one south and the other north, and each distant about a mile." These veins of "bitumen" can be nothing other than the substance now known as gilsonite. Veins of "asphalt" in the same locality are mentioned briefly by Endlich (1876). The term "gilsonite" commemorates Samuel Gilson who pioneered the commercial use of the substance in the 1880's.

The gilsonite veins are located a short distance south of the synclinal axis of the basin, and their strikes, if extended, would intersect the synclinal axis at acute angles. The veins occur in groups that trend approximately parallel to one another, and within the groups veins are nearly parallel. The three principal groups of veins are located in the vicinity of Bonanza on the north bank of the White River, in the vicinity of Rainbow about 10 miles south of the White River, both of these localities being near the Utah–Colorado state line, and in the Myton–Fort Duchesne district about 40 miles to the west.

The gilsonite veins range from small deposits an inch or so in width and a few feet in length to large deposits several feet in width and several miles in length. The Cowboy Vein in the Bonanza Group has a maximum width of 18 ft, an outcrop length of about 7 miles, and has been mined to a depth of about 900 ft. The Rainbow Vein in the Rainbow Group has a maximum width of 10 ft, an outcrop length of about 16 miles, and has been mined through a vertical distance of several hundred feet. The Cowboy and Rainbow Veins are two of the largest deposits. There are many smaller veins.

The gilsonite veins are remarkable for their nearly uniform features. They are nearly straight, extending across the country in lines almost as if laid out by transit. The walls are surprisingly smooth and do not deviate from the vertical by more than about 5°. In mining operations the gilsonite breaks clean from the walls leaving smooth sandstone faces. The vein material generally is pure bitumen. Horses and fragments of wall rock occasionally occur in some veins and apparently do not occur in others. Some horses have been found suspended in the gilsonite only a few feet from the places where they were broken from the walls.

Most of the known gilsonite veins occur in massive sandstones of the Uinta Formation. Some of them increase slightly in width with depth and others maintain a nearly uniform width. Near the base of the sandstones the veins become narrower and then feather out into a large number of veinlets, stringers, and nodules in the shales and marlstones of the upper part of the Green River Formation. The "veinlets" or "roots" can be traced downward until finally they reach the apparent source of gilsonite in the rich oil shales of the Parachute Creek member of the Green River Formation. The feathering out of large gilsonite veins into Green River Shales can be observed where veins of the Bonanza Group are exposed on the north wall of the White River Canyon and where the Rainbow Vein crosses some of the canyons tributary to Evacuation Creek. In some localities the dispersed veinlets pass through the oil shales, then coalesce to form large gilsonite veins in massive sandstones at the base of the Green River Formation and in the upper part of the Wasatch Group.

The Rainbow Vein system is an excellent example of the existence of gilsonite both above and below its apparent source in the oil shales. The northwest end of the vein crops out in massive sandstones of the Uinta Formation. This section of the vein has been mined over a distance of several miles with the workings extending downward to where the main vein branches into the Green River Shales. Toward the southeast the vein outcrop appears in successively lower units of the stratigraphic section. The middle part of the outcrop is in oil shales and paper shales of the Green River Formation and appears as a large number of narrow veinlets and stringers. There must be some continuity of veinlets through the shales although most of those appearing on the outcrops terminate upwards, downwards, or both, within the shales. For a distance of about 3 miles near the southeast end of the vein its outcrop is in massive sandstones at the base of the Green River Formation. The southeast end of the vein is in the Wasatch Group. The portal of the abandoned Dragon mine is in sandstone near the base of the Green River Formation. This mine was worked to a depth of at least two hundred feet and apparently below the base of the Green River Formation. The vein terminates downwards in clays and mudstones of the Wasatch Group.

The Weaver–Colorado Vein that is southeast of the Bonanza Group, and which may be an extension of the Wagon Hound Vein of that group, has an outcrop about seven miles long. Almost all of this length is in lower Green River and upper Wasatch strata and below the apparent oil shale source beds.

The Rainbow and Weaver–Colorado gilsonite veins are the only ones that have been eroded to such depths that their basal sections below the oil shales are exposed. The outcrops of all other known veins are in Upper Green River, Uinta, or Duchesne River strata. There has been no exploration of these veins by mining or drilling below the Green River Shales, therefore, it is not known whether or not they have extensions below the oil shales. The presence of massive sandstones below the oil shales is favorable for the existence of large veins while the presence of clays and shales is unfavorable.

There has been considerable controversy concerning the origin of the fissures occupied by the gilsonite. There has been essentially no displacement of strata, either vertically or horizontally, along these fissures. In the mined out parts of the veins stratification features can be followed along both walls with no indication of displacement. The most reasonable explanation appears to be that the fissures are large tension cracks formed during down-warping of the basin following deposition of the Green River and Uinta sediments.

Gilsonite commonly has not penetrated the wall rocks except along those parts of the veins close to the oil shales, and below them. Reports differ considerably on this matter, some observers having claimed that gilsonite-saturated wall rock is the prevalent condition, while others have stated it to be the exception. The viewpoints probably depend upon what parts of the veins were examined. Along those parts of the veins that are about four or five hundred feet or less above the source beds in the oil shales, gilsonite commonly has penetrated the wall rocks; thus along the part of the Rainbow Vein system in the Uinta Sandstone the wall rock in many places is saturated with gilsonite to distances of several feet from the vein. Gilsonite also has penetrated the sandstone along the walls of minor fractures, some of which extend a few hundred feet from known major veins. Along the southeastern part of the Rainbow Vein system that is in the lower Green River and Wasatch Sandstones most of the wall rock has been penetrated by the gilsonite. The same condition exists along the part of the Weaver–Colorado Vein that is in lower Green River Sandstone. Gilsonite has penetrated the wall rocks very little, if at all, along those parts of the veins that are more than about 500 ft above the source beds; thus the wall rocks along the outcrops of veins in the Bonanza and Myton–Fort Duchesne Groups, for the most part, have not been penetrated at all by gilsonite. Miners who have worked the deeper parts of these veins, at depths of about 700 ft or more below the surface, state that here gilsonite quite commonly has penetrated the wall rock.

The physical and chemical characteristics of gilsonite are variable from one part of a vein to another and from vein to vein. In general, the gilsonite occurs as a solid homogeneous mass that breaks with a conchoidal fracture. In the marginal parts of some veins it has a fine columnar structure perpendicular to the walls. This gilsonite is called "pencillated ore" and may occur on one or both walls of a vein. The homogeneous gilsonite in the interior of a vein generally has a lower fusing point, slightly lower specific gravity, higher solubility in organic solvents, and more lustrous appearance than the material close to the walls. For commercial purposes, gilsonite from the interior of the vein is classified as "selects" and that from the margins as "seconds". The proportions of "selects" and "seconds" vary between different veins and different parts of the same vein. Some of the narrower veins consist only of "seconds", and gilsonite near the outcrops of almost all of the veins may be entirely "seconds". It is possible that some kind of weathering action may be responsible for the difference. Gilsonite in thin veins, along the walls of thick veins, and at the outcrops may have become slightly more polymerized than that in the interior of thick veins, or it possibly may have taken up oxygen to become slightly oxidized.

Plastic and liquid phases of gilsonite occasionally are found in some of the deeper mines such as those in the Tabor Vein of the Bonanza Group and the Castle Peak Mine near Myton. In some places these soft varieties of gilsonite are found within the veins and in some places they seep from fractures and porous parts of the wall rock. "Liquid gilsonite" was found at a depth of about 1900 ft in well No. 1 Jensen located in W 1/2 NE 1/4 sec. 21, T. 8 S., R. 16 E., Salt Lake Meridian.

Tabbyite. Tabbyite is a bitumen occurring in veins along Tabby Canyon. This locality is between the gilsonite and wurtzilite areas. The veins range from small stringers to deposits from which several tons of material have been Mined. The tabbyite veins occur in lacustrine beds near the top of the Green River Formation, and the source of the bitumen appears to be in oil shale beds of this part of the section.

Wurtzilite. The pyrobitumen wurtzilite occurs in veins in an oil shale zone of the lacustrine facies of the Uinta Formation. The wurtzilite deposits appear to be restricted to a stratigraphic interval of about 50 ft and are located in the area including Indian, Lake, and Sams Canyons in the western part of the Uinta Basin.

The oil shales containing the wurtzilite were deposited near the end of the life of Lake Uinta when it had become greatly reduced in size and its waters were highly saline and apparently were strongly sulfurous in their deeper parts. These "oil shales" are hard, tough, marlstones with semiconchoidal fracture and little tendency to split along bedding planes. The strata above and below the oil shales are much softer and consist of thin-bedded shales and sandy shales that part readily along bedding planes.

The sizes of the wurtzilite veins have been closely controlled by the enclosing strata. The wall rock oil shales are also the source beds of the wurtzilite. These hard marlstones are characterized by joints cross-cutting the stratification and few fractures along bedding planes. Open, nearly vertical fissures, are therefore, common. The adjacent shaly strata are characterized by bedding plane fracture, therefore, the open fissures within the marlstones terminate abruptly near the shale contacts. The vertical dimensions of the wurtzilite veins are limited to the thickness of the marlstones and generally are in the range of from 15 to 30 ft. The veins range from a fraction of an inch to a maximum of about 2 ft in width, and from a few feet to several thousand feet in length. The largest known vein is located along the southeast wall of Right Fork of Indian Canyon and has a length of nearly 3 miles.

Some of the wurtzilite veins are branched, have off-sets, and are quite irregular in form. This condition results from a local block-like fracture pattern in the marlstone. Quite unlike gilsonite, wurtzilite has a tendency to cling to the wall rock and does not break "clean". This property resulted in considerable waste in mining because the wurtzilite could not readily be separated from the rock.

Although some of the wurtzilite veins are large, possible variations in the properties of the pyrobitumen are not apparent by visual examination. Wurtzilite occurs as an apparently homogeneous mass having conchoidal fracture, and generally is free from included wall rock fragments. Near the north edge of the wurtzilite area a semi-plastic bitumen seeps from fractures in the oil shale zone. This substance, sometimes called "liverite", has essentially the same chemical properties as wurtzilite and is considered to be a fluid phase of it.

Fracture control of the bitumen deposits. The solid bitumens of the Uinta Basin apparently have been squeezed into fissures, probably by the compaction of the sediments. The size and complexity of the fissures were determined partly by the physical characteristics of the rock that was ruptured and partly by their location with respect to the synclinal axis of the basin. In general, large, simple fissures developed in the massive, thick-bedded sandstones and marlstones, and small, irregular fracture systems developed in the thin-bedded shales and the clays. The larger fissures were developed closest to the synclinal axis and roughly parallel to it.

The major fractures of the Uinta Basin were formed as the area was warped following deposition of the Green River and most of the Uinta sediments. The large fissures occupied by the gilsonite and wurtzilite veins, and possibly the smaller fissures occupied by tabbyite and albertite veins, are generally considered to be tension cracks. Some of the fracture zones in the gilsonite area are known to extend from the upper part of the Wasatch beds through the Green River and Uinta Formations and into the Duchesne River beds where these are present.

The massive, thick-bedded sandstones, presumably under tensional stresses, ruptured at a few places to form great vertical fissures. The thickest sandstone sections are in the fluviatile facies of the Green River and Uinta Formations in the northeastern part of the basin. Here, the fissures now occupied by the gilsonite veins, extend from the bottom to the top of the sandstone strata. In the Uinta Formation this distance exceeds a thousand feet. In the basal sandstones of the Green River Formation it ranges up to about 400 ft. The great fissures in the sandstones, upon passing into the thin-bedded, fine-grained sediments, quickly split into a myriad of small fractures, most of which are vertical or nearly so, but some of which follow bedding planes. The fracture zones terminate both upwards and downwards in soft clays and mudstones. The large, gilsonite-filled fissures do not persist for more than a few tens of feet after passing from the sandstones. The outcrop of the Cowboy Vein of the Bonanza Group can be followed to the northwest to a point where it feathers out in clays resting upon the sandstone. The outcrops of the Weaver-Colorado and Rainbow Veins can be followed to the southeast to points where they feather out in Wasatch mudstones immediately underlying Green River sandstones.

The thin-bedded marlstones, paper shales, and clays of the lacustrine facies responded to tensional stresses by bedding plane slippage and closely spaced vertical fracturing. The vertical fractures are most abundant in the harder sediments, such as marlstones and limestones, and tend to terminate rather abruptly against adjacent softer shaly strata. These fractures commonly are restricted in the vertical dimension by the thickness of a hard limestone or marlstone zone.

The albertite and wurtzilite areas are within parts of the basin in which the stratigraphic sequence consists almost wholly of lacustrine sediments, most of which are thinly-bedded. These areas are located on the southwest flank of the basin, and, therefore, the rocks were not subjected to the maximum tensional stresses during down-warping of the basin. The tension cracks are considerably smaller than those of the gilsonite area and tend to be restricted to the harder limestone and marlstone zones. Because the vertical fractures mostly end abruptly against softer shales and clays, the albertite and wurtzilite veins are restricted to rather short stratigraphic intervals that include the respective oil shale source beds of these pyrobitumens. Offsets and horizontal branches of these veins are rather common because even the dense marlstones occasionally part along bedding planes, especially those that happen to be somewhat shaly or silty.

Source and Emplacement of the Bitumens. A significant feature of the Uinta Basin bitumens is that, although several varieties are found in the area, each variety is restricted to a particular stratigraphic interval, or occurs in veins that have their roots within a particular stratigraphic interval. Hunt and others (1954) have shown that the soluble organic material extracted from the various source beds has the same composition, as indicated by infrared analyses and refractive indices, as the bitumens in associated fractures and saturated sands. These facts indicate that the composition of the organic source material in different stratigraphic intervals was a major factor in determining the kind of bitumen that separated from them. Highly paraffinic oil and ozocerite, which appear to have the same source, occur in beds of Wasatch age around the margins or in oil shales presumably of the same age in the center. Known deposits of albertite and ingramite are very local in their occurrence and are associated with oil shale beds in the lower part of the Green River Formation. The source beds of gilsonite and tabbyite are the rich oil shales of the middle part of the Green River Formation. The bituminous sandstones, for the most part, belong to fluviatile and shore-line facies of the Green River Formation that interfinger with the lacustrine facies and its rich oil shales. The stratigraphic interval of the bituminous sandstones is above that of albertite and overlaps the lower part of the gilsonite interval. The infrared spectra of organic extracts from the bituminous sandstones generally are similar to that of gilsonite, but a few of them resemble wurtzilite (Hunt *et al.*, 1954). The source beds and stratigraphic interval of the wurtzilite are the oil shales near the top of the lacustrine section in the Uinta Formation.

The two factors that most influenced the composition of the organic constituents of the oil shales were the salinity and toxicity of the Uinta Lake water. During early Tertiary time the climate of the area was warm and humid, and a temperate to semi-tropical fauna and flora flourished (Bradley, 1931; Berry, 1925). Initially, during Wasatch time, the lake water was fresh and aerated throughout, this being a condition that permitted large numbers of benthonic organisms to thrive. Near the beginning of Green River time the basin became permanently closed and then the lake water became increasingly saline. This condition is indicated by the deposition of calcitic limestone in the basal sediments (Wasatch), followed by chert, calcite, and dolomite (lower Green River), calcite, dolomite, and nahcolite (middle and upper Green River), and finally dolomite and highly soluble alkali–alkaline earth carbonates in the uppermost sediments (Uinta). During early Green River time the lake became chemically stratified, at first intermittently, and then permanently, with the upper layer being aerated and supporting abundant life while the bottom layer was stagnant and sulfurous. This condition is indicated by the disappearance of benthonic fossils and by the presence of abundant sulfide minerals in certain beds. The concurrent increase in salinity and toxicity was subject to many fluctuations but generally was continuous from the closing of the basin to the end of life of Lake Uinta.

As the salinity and toxicity of the lake water increased, the character of the bitumens changed. Thus, ozocerite consists mainly of paraffin hydrocarbons and contains only traces of nitrogen and sulfur. Albertite, which is associated with sediments deposited in a very mildly saline environment, consists mainly of aromatic ring compounds and contains only slightly more nitrogen and sulfur than ozocerite. Gilsonite, the source beds of which were deposited in a rather strongly saline environment, is predominately aromatic and naphthenic and contains up to about 2% each of nitrogen and sulfur. Wurtzilite, derived from source beds deposited in a highly saline and toxic environment, is naphthenic in character and has a high sulfur content that ranges up to about 7%, but it has less nitrogen than gilsonite.

The aquatic life that flourished in Lake Uinta changed, both as regards species and relative abundance of various species, as salinity of the water increased. Fossil evidence of this condition shows a transition from a varied fauna and flora including an abundance of macrofossils in the basal lacustrine beds to an assemblage of lower orders of life represented mainly by microfossils in the middle and upper lacustrine beds. Fossil fish are found in certain marginal facies. The oil shales themselves are usually barren of any higher forms of life. That the composition of organic matter in successively younger oil shales changed simultaneously with the salinity and the fauna and flora of the lake is indicated by the composition of soluble material that can be extracted from them. It is probable that the character of the bitumens is dependent in part upon the kinds of life that furnished the source organic material and in part upon the action of saline constituents in the water in preserving this material.

The process by which both solid and viscous semifluid bitumens associated with oil shales were formed from indigenous organic matter is unknown. The many geologists who have examined the bitumen deposits associated with the Uinta Basin oil shales are in general agreement that these substances moved into the fissures, cavities, and porous rocks while in a fluid, although viscous condition. The fluids might have been essentially syngenetic constituents of the sediments, or they might have been formed from the organic matter by some chemical process. These observations apply equally well to the Albert Shale and the associated albertite.

Although oil shales and kerogen-rich rocks exist in many parts of the world, solid bitumens are associated with only a few of them. The oil shale formations that are source beds for the solid bitumens have, in common, some significant characteristics: (1) they include thick strata having exceptionally high organic contents and may yield on retorting from about 40 to as much as 100 gallons of oil per ton of rock; (2) they have been buried under several thousand feet of cover; (3) they have been folded during the course of regional deformation; (4) large fissures developed in the oil shales and adjacent rocks during the folding; (5) they have been subjected to considerable compaction, both from the weight of overlying sediments and from pressures developed during folding. On the other hand, oil shales that have not been source beds for solid bitumens generally have these characteristics: (1) their content of organic matter is relatively low, but there are some exceptionally rich oil shales in this group; (2) they have been buried under thin covers of sediments ranging from a few tens to a few hundreds of feet thickness; (3) they have not been folded and lie nearly horizontally or with slight regional dips; (4) they have not been subjected to appreciable compaction.

The features enumerated above may explain why many oil shale formations, such as the Chattanooga and its correlatives in the United States and the Cambrian–Ordovician shales of the Baltic region of Europe, have not given rise to deposits of solid bitumens. The Chattanooga is a "lean" oil shale in comparison with the Green River and Albert Shales, and it has not been folded. The Cambrian–Ordovician Shales of the Baltic region include some rich oil shale strata, but these formations lie nearly horizontal, have never been buried under a thick cover, and have not been subjected to profound compaction. The Dictyonema and Kukersite Shales of the eastern Baltic region apparently have given rise to no solid bitumens, at least the authors have found no reference to such substances in the available literature. In the Billingen–Mosseberg area, Västegötland, Sweden, small veins of a bitumen having the physical characteristics of gilsonite occur in oil shale and blue clay at a depth of about 100 m below a thick diabase sill (Dr. T. Bertil Dahlman, Geological Survey of Sweden, oral communication). The oil shale in this locality is very "lean", and it is thought that much of the original organic matter was distilled out by heat from the igneous intrusion, and that the veins of bitumen were formed at the same time. Bitumen veins are not known to be associated with oil shales in other areas of Sweden.

There is no evidence of former thermal activity in the Uinta Basin and in the vicinity of the Albert Shales that can be attributed to igneous intrusions. Temperatures that have existed within these oil shales have been determined by the geothermal gradient and depth of burial. Within the Uinta Basin a rough estimate places the maximum temperature that existed in the albertite zone, buried at a depth of about 6000 ft, at about 140°F, and in the wurtzilite zone, buried at a depth of about 2000 ft, at about 90°F. Maximum temperatures that have existed within the Albert Shales probably fall within this range. These temperatures are insignificant as a cause of pyrolysis; therefore, this process can be eliminated as playing any significant role in the genesis of the bitumens.

The authors believe that the mechanism by which the bitumen deposits moved from their shale source beds into the fissures was probably viscous flow under the differential pressure set up by the opening of the fissures. The fluids must have been viscous because the bulk of this material remained in the fissures and only minor amounts of it penetrated porous wall rocks. The bitumens that occupy the fissures are probably from 1 to 5% of the organic matter in the shales that is soluble, rather than from the insoluble kerogen. Comparisons of the composition of this soluble material extracted from the oil shales show it is similar to the bitumens in the associated veins (Hunt *et al.*, 1954). It has been calculated that only 1%

of the organic matter in shales adjacent to the gilsonite veins would more than fill these veins. Initially these bitumens were buried under a pressure equivalent to a depth varying from possibly 6000 ft for albertite, to 2000 ft for wurtzilite. As the area was uplifted, tensional cracks developed tending to create reduced pressure voids into which the bitumens moved. The bitumens moved as viscous fluids and subsequently became solids through inspissation, polymerization, oxidation, or some combination of these processes.

The bitumen deposits undoubtedly were formed simultaneously with the fissures that they fill. It is inconceivable that tremendous fissures, such as those occupied by the gilsonite deposits, could have existed for any length of time without becoming filled with debris from the soft shales, clays, and slightly indurated sands that determine their upper limit. The principal fissures were formed as the basin warped following deposition of the lacustrine sediments and was coincident with uplift in the surrounding Wasatch and Uinta Mountains and Uncompahgre Plateau. The upper parts of the St. Louis and Fort Duchesne gilsonite veins near Fort Duchesne are in the Duchesne River Formation. These fissures could not have been formed earlier than in late Oligocene time. They most likely are of Miocene age, that is, they were formed during the Laramide orogeny. There are no features indicating that there was more than one period of major fracturing of the Tertiary formations of the Uinta Basin, therefore, it is probable that all of the bitumen deposits are of about the same age.

Composition of the Bitumens of the Uinta Basin

Types and classification of bitumens—Bituminous substances are generally divided into two major classes, those soluble, and those insoluble, in carbon disulfide (Abraham, 1945). Subdivisions of these major classes are made on the basis of the fusibility of the substance. In Fig. 3 is presented a classification of most of the known types of naturally occurring bitumens. The crude oils and oil seeps are low molecular weight, volatile bitumens, whereas all the rest of the substances are high molecular weight, nonvolatile bitumens. Going across the chart from left to right there is a decrease in the solubility and an increase in the fusion point and the carbon to hydrogen ratio of the bitumens.

Ozocerite is a mineral wax composed principally of straight chain paraffin hydrocarbons with a few naphthenes. Hatchettite and scheererite are local names for varieties of ozocerite found in Scotland and Switzerland. Montan wax is a mixture of high molecular weight acids and esters in the range from about C_{29} to C_{35}. It is not found in a free state but is extracted from lignite or pyropissite by solvents. Ozocerite is the only mineral wax found in the Uinta Basin. It is called Utah wax in the literature to distinguish it from Galician ozocerite.

Viscous liquids or solid low-melting bitumens are classified by Abraham as asphalts. The asphalts that are readily extracted from asphaltic sandstones and limestones also come under this classification. Among the asphalts found in the Uinta Basin are: tabbyite, a solid found in veins in Tabby Canyon; a semi-solid bitumen oozing from a creek bed west of Duchesne and called "liverite" in this paper; liquid gilsonite found at depths in the Bonanza gilsonite mine; and argulite, an asphalt saturating sandstone in the canyon of Argyle Creek south of Ouray. There are also asphaltic limestones north of Colton and asphaltic sandstones at many other places in the basin. Some of these contain up to 50% asphalt by volume.

An asphalt with a fusing point higher than 230°F is classified as an asphaltite. Gilsonite is the only asphaltite found in the Uinta Basin.

Bituminous substances that decompose before they melt are called pyrobitumens. The asphaltic pyrobitumens are differentiated from the non-asphalts or coals, in that the former generally contain less than 5% oxygen. Wurtzilite, "ingramite", and albertite (also called nigrite) are the principal asphaltic pyrobitumens found in the Uinta Basin.

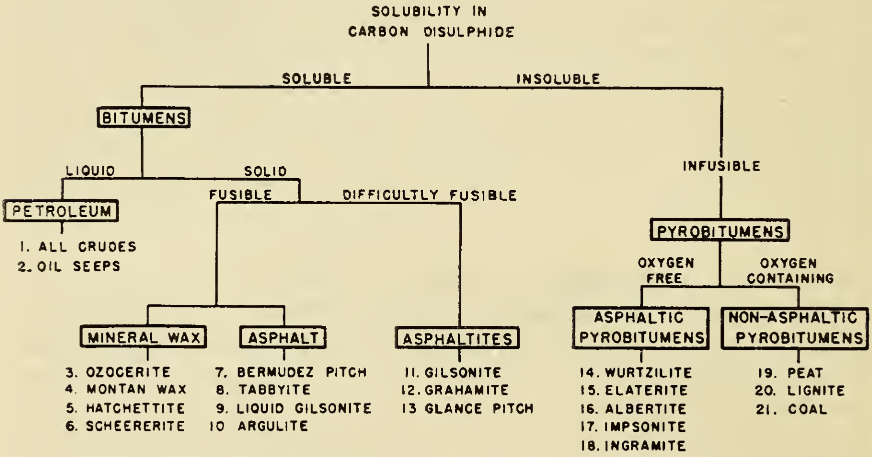

FIG. 3. Terminology and classification of naturally occurring hydrocarbons (adapted from H. Abraham, 1945).

The bitumens listed in Fig. 3 can be separated into fractions on the basis of their solubility in organic solvents. When the bitumen is mixed with petroleum ether it separates into a soluble portion (malthenes) and an insoluble portion (asphaltenes). The malthenes can be further subdivided by mixing them with adsorbent clay and extracting with carbon tetrachloride. The extracts are the oily constituents and the residues are the asphaltic resins. The resins are removed from the clay with carbon disulfide. When the asphaltenes are mixed with carbon disulfide they separate into a soluble portion (carbenes) and an insoluble portion (carboids).

Physical and chemical properties—*General properties.* The different bitumens of the Uinta Basin vary considerably in their physical and chemical properties which provide a means for characterizing and identifying them. Table 1 shows the variation in solubility, fusing point, specific gravity, fixed carbon content, and elemental analysis. The bitumens are arranged in order of increasing fusing point: waxes, asphalts, asphaltites, and pyrobitumens. The fusing points increase rapidly for the denser bitumens. Different grades of gilsonite range in fusing point from 230 to 350°F. Solubilities in carbon disulfide show a sharp break between the soluble asphaltite, gilsonite, and the insoluble pyrobitumen, wurtzilite.

The fixed carbon content is defined as the carbon residue left after heating the bitumen at 950°C for 7 min in the absence of air. It is useful in making a preliminary classification of the bitumen. In general it stays within definite limits for the different types of bitumens. Some of the fixed carbon analyses made on Uinta Basin samples are listed in Table 2. These values are on an ash-free basis.

TABLE 2

Fixed Carbon Analyses of Uinta Basin Bitumens

Bitumen	Source	Wt. % carbon residue*
Ozocerite	Soldier Summit	4.1
Wurtzilite	Country Gentlemen	5.9
Wurtzilite	Powtin Vein	6.2
Wurtzilite	Canyon Junction	7.6
Ingramite	Soldier Summit	8.1
Ingramite	Soldier Summit	8.4
Gilsonite	Black Dragon	13.8
Gilsonite (pencillated)	Bonanza	16.3
Gilsonite	Bonanza	16.6
Gilsonite	Weaver	18.6
Albertite	Soldier Summit	38.0
Albertite	Soldier Summit	37.7

* Ash-free basis.

Albertites are readily distinguished from the other bitumens by their high carbon residues. Different types of gilsonites differ only by a few per cent in their carbon residues. Wurtzilites and ingramites have unusually low residues considering the fact that both are pyrobitumens.

The refractive index of a bitumen is useful as a correlation index and as an indication of molecular structure. Within any one molecular weight range, the order of increasing refractive indices is paraffins, naphthenes, aromatics. In the high molecular weight ranges there is some overlap but the rule still applies generally. Figure 4 is a frequency distribution chart of the refractive indices of ninety bitumen samples. These samples were chosen from as many different localities as possible so as to obtain a completely random distribution. The length of each bar in Fig. 4 indicates the number of samples having that particular refractive index. It is apparent that with refractive indices alone it is possible to distinguish between albertite, gilsonite, wurtzilite, and ozocerite, except for indices between 1.585 and 1.595 where gilsonite and wurtzilite overlap. It is not possible to distinguish between ingramite, wurtzilite and tabbyite by refractive index since all three overlap each other.

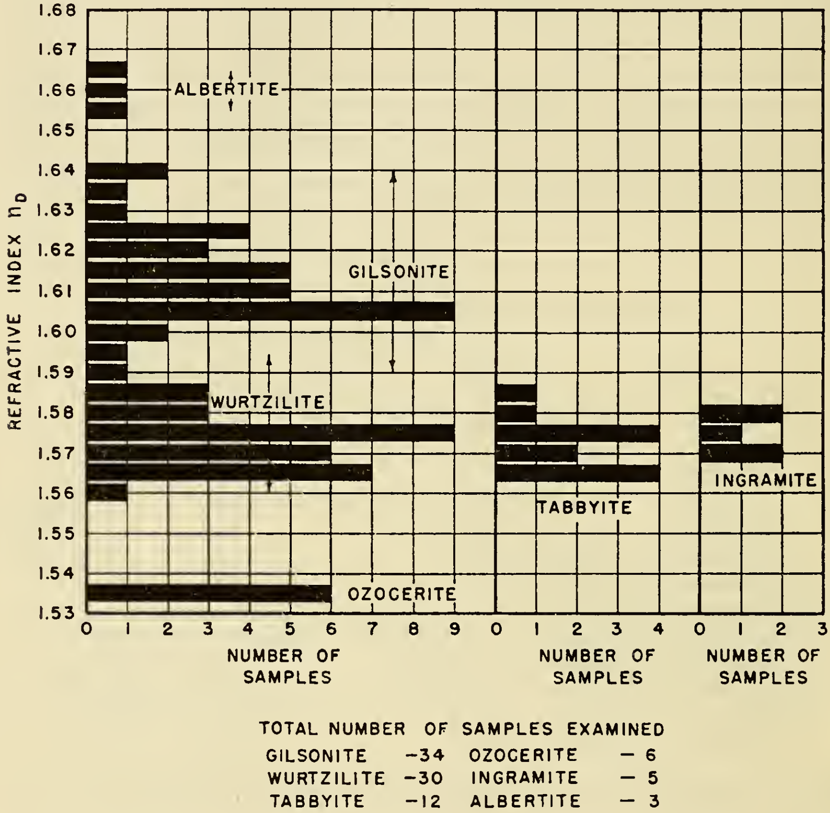

FIG. 4. Frequency distribution of the refractive indices of Uinta Basin bitumens.

When the median refractive index of the bitumens is plotted against fixed carbon content, the points fall in a smooth curve as shown in Fig. 5. Ozocerite, with a high paraffin content, has a low refractive index and carbon residue. At points higher on the curve, where the indices and carbon contents are high, there is a decrease in the paraffin content and an increase in the aromatic and condensed ring structures. The position of the two pyrobitumens, wurtzilite and ingramite, at the low end of the curve strongly suggests that they either have fewer aromatics in their structure, or smaller molecular units than either gilsonite or albertite. There is also other evidence to support this, such as the carbon to hydrogen ratios. Ratios for wurtzilite and ingramite, as will be shown later, indicate these bitumens have more hydrogen per molecule than gilsonite or albertite. Since paraffin and naphthene structures have more hydrogen than aromatics, it is evident that wurtzilite and ingramite contain more of the former structures than gilsonite and albertite.

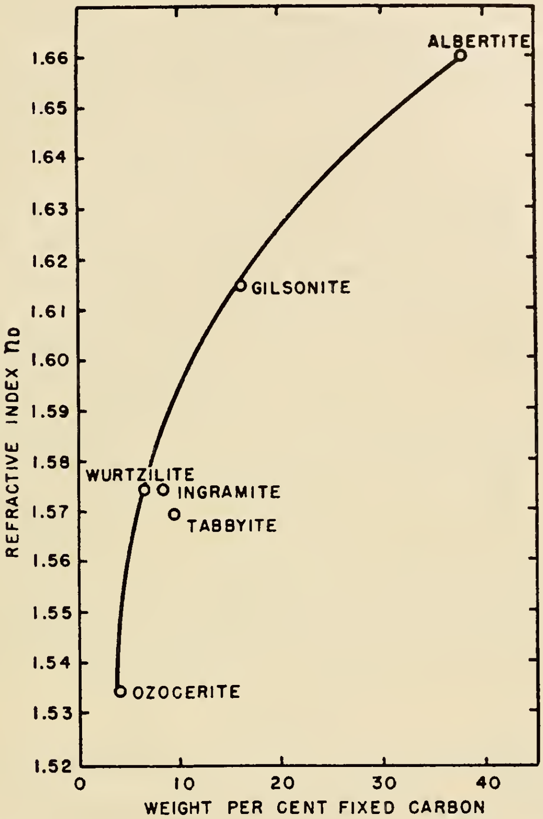

FIG. 5. Refractive index and fixed carbon content of the Uinta Basin bitumens.

Structure correlations from infrared absorption spectra. Additional information on organic structures of bitumens can be obtained from a study of their infrared spectra. Specific atomic configurations, such as an —OH, >C=O, and phenyl groups, have absorption bands in specific narrow regions of the spectrum. For example, the —OH group of alcohols absorbs at a wave length of 3.0 μ, the >C=O of ketones, aldehydes, and acids at about 5.9 μ, oxygenated structures in the region of 8–10 μ, aromatic structures from 11 to 13.5 μ, and long chain aliphatic paraffins around 13.9 μ. The ratios of aromatic and paraffinic structures can be compared among bitumens from the intensity of absorption bands in the 11–13.5 μ aromatic region and in the 13.9 μ paraffin region. A considerable amount of data on the correlation of atomic groups and infrared absorption frequencies has been reported in the literature (Faraday Society, 1945;

Barnes *et al.*, 1948; Randall *et al.*, 1949). In general, the order of compounds having increasing intensities of absorption bands is naphthenes, paraffins, olefins, aromatics, oxygen, sulfur, and nitrogen compounds. The nonhydrocarbons have absorption bands approximately twenty times more intense than paraffin hydrocarbons.

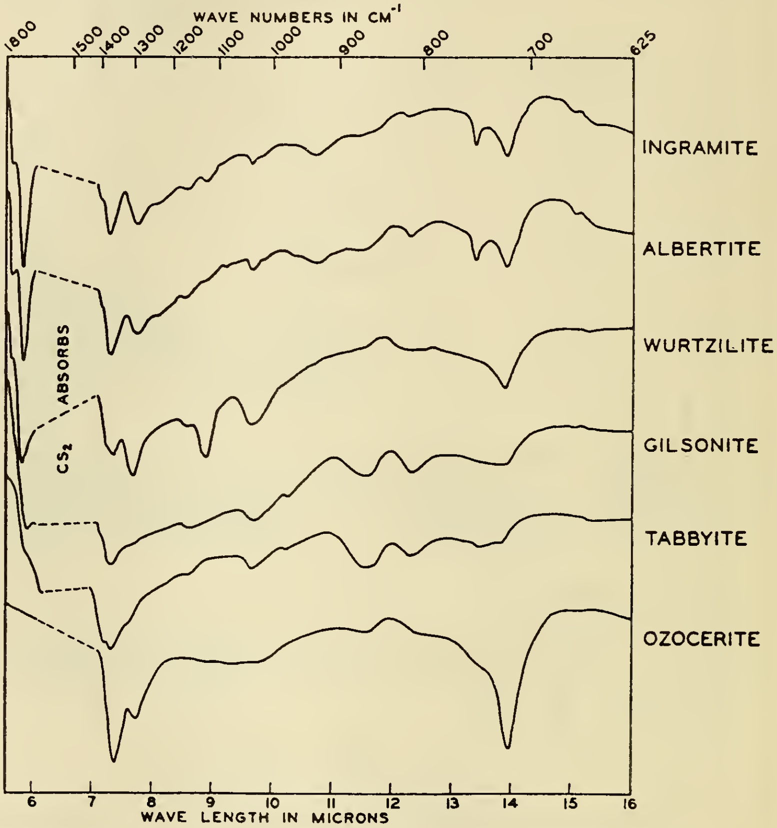

FIG. 6. Infrared spectra of bitumens, Uinta Basin.

Structures in the carbon disulfide soluble portions of the Uinta Basin bitumens can be determined by examination of the curves in Fig. 6. The absorption peaks at 13.9 μ in the spectra of ozocerite, wurtzilite, albertite and ingramite indicate the presence of chains of five or more carbon atoms in these compounds. The sharp peaks at about 13.4 μ in the ingramite and albertite spectra are attributed to polycyclic aromatics. The two broad humps at 11.5 and 12.3 μ are due to aromatics, the latter peak being attributed to para-substituted aromatics. The peaks at 8.6 and 8.65 μ in the spectrum of gilsonite, and at 8.9 μ in the spectrum of wurtzilite, are probably due to oxygenated compounds which absorb strongly in the 8–10 μ region. The sharp peaks at about 5.9 μ in the spectra of ingramite and albertite are due to the >C=O group.

The liquid bitumens of the Uinta Basin have essentially the same basic structures as the soluble portion of the solids. Evidence for their similarity in basic structures is provided by the similarity of their infrared spectra. In Fig. 7 the spectra of liquid, semi-solid, and the soluble portion of solid forms of gilsonite and wurtzilite type bitumens are shown. The gilsonites are all from the Bonanza Vein system. F-79 is a liquid ooze from a gilsonite mine, and the others are harder forms of gilsonite with increasing asphaltene content. It will be noted that all of the first four spectra are characteristic of gilsonite (Fig. 6). Their chief differences are in the 8–10 μ range where the increasingly harder forms show increasing absorption due to the presence of oxygenated compounds. They are distinctly different from the spectra of wurtzilite-type bitumens (F-313 and F-1100). Sample F-313 is a semi-solid material that is completely soluble in CS_2, and F-1100 is a true wurtzilite that is only partially soluble. Both show the characteristic wurtzilite curve with strong absorption at 8.9, 9.65, and 13.9 μ.

Elemental analyses. Some information about the molecular structures of bitumens from the Uinta Basin can be obtained from an analysis for the elements carbon, hydrogen, sulfur, and nitrogen. The ratio of hydrogen to carbon atoms varies in different hydrocarbon structures. Naphthene and paraffin hydrocarbons have high H/C ratios, whereas condensed aromatics have low H/C ratios. Consequently, bituminous substances rich in the former structures have high H/C ratios, whereas carbonaceous substances rich in the latter have low H/C ratios. Ozocerite, a paraffin wax, has the highest H/C atomic ratio of the Uinta Basin bitumens, whereas albertite, the pyrobitumen, has the lowest ratio next to the coals. The ratios of these and other natural bitumens are listed in Table 3.

TABLE 3

Hydrogen to Carbon Atomic Ratios for Natural Substances

Substance	Source	Atomic H/C ratio
1. Ozocerite	Soldier Summit	1.96
2. Ozocerite	Miller Mine	1.89
3. Tabbyite	Tabby Canyon	1.62
4. Ingramite	Soldier Summit	1.62
5. Wurtzilite	Indian Canyon	1.60
6. Wurtzilite	Red Creek	1.59
7. Gilsonite	Black Dragon	1.47
8. Gilsonite	Bonanza	1.45
9. Gilsonite	Rainbow	1.42
10. Albertite	Soldier Summit	1.32
11. Albertite	Albert Co., New Brunswick, Canada	1.24
12. Coal	Uinta Basin	0.99
13. Bituminous Coal		0.80
14. Anthracite		0.56

The order in which the substances are listed in Table 3 represents an order of decreasing paraffinicity and increasing aromaticity.

Structural interpretations based on H/C ratios are valid only if the total quantity of nitrogen, sulfur, and oxygen in the substances being compared does not differ appreciably. Since these elements replace hydrogen, a pure hydrocarbon structure would have a higher H/C ratio than a corresponding structure containing N, S, or O. Maximum differences in the N, S, O content of the Uinta Basin bitumens are about 6%, which is too low to influence the order in Table 3. The Uinta Basin coal, and bituminous coal, with a high (10–15%) N, S, O content, would have H/C ratios closer to 1.28 and 1.05, respectively, on a N, S, O free basis.

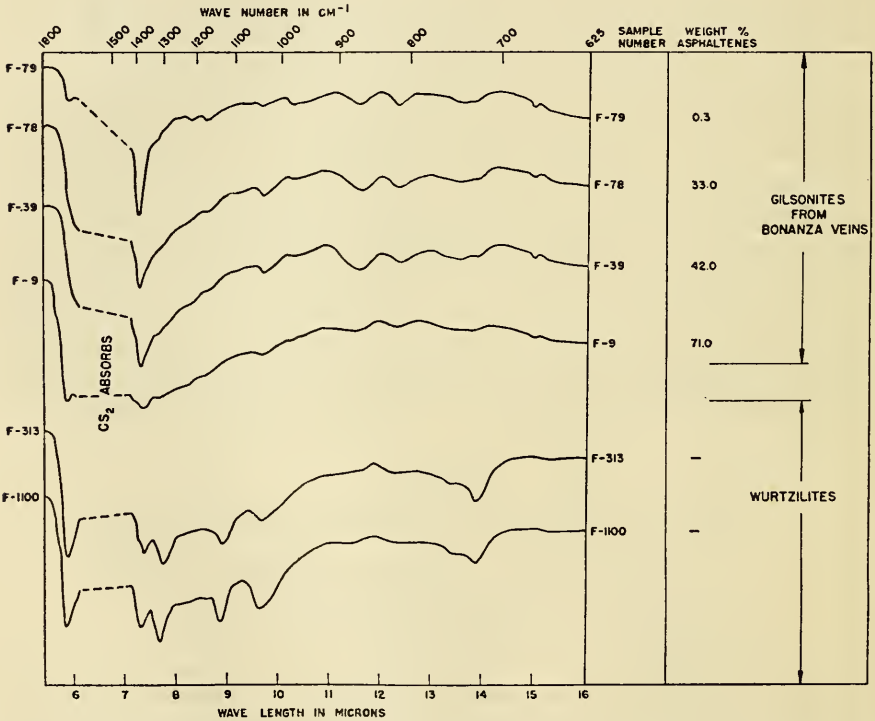

FIG. 7. Infrared spectra of liquid and solid bitumens, Uinta Basin (in CS_2 solution).

The bitumens with low H/C ratios are generally more insoluble and infusible than those with high H/C ratios. Wurtzilite is a notable exception to this rule having a higher H/C ratio than gilsonite, but being more insoluble. Solubility and fusibility are influenced by other factors, such as the sulfur, nitrogen, and oxygen content of the bitumens.

The sulfur and nitrogen contents of the Uinta Basin bitumens are shown in Fig. 8. Wurtzilite has the highest sulfur content, by far, of the entire group, averaging about ten times as much sulfur as gilsonite. The presence of sulfur linkages in the wurtzilite structure is believed to lead to its rubbery properties and its insolubility and infusibility. Sulfur is known to cross-link large hydrocarbon molecules, as in natural or synthetic rubber, imparting rigidity and insolubility to the material.

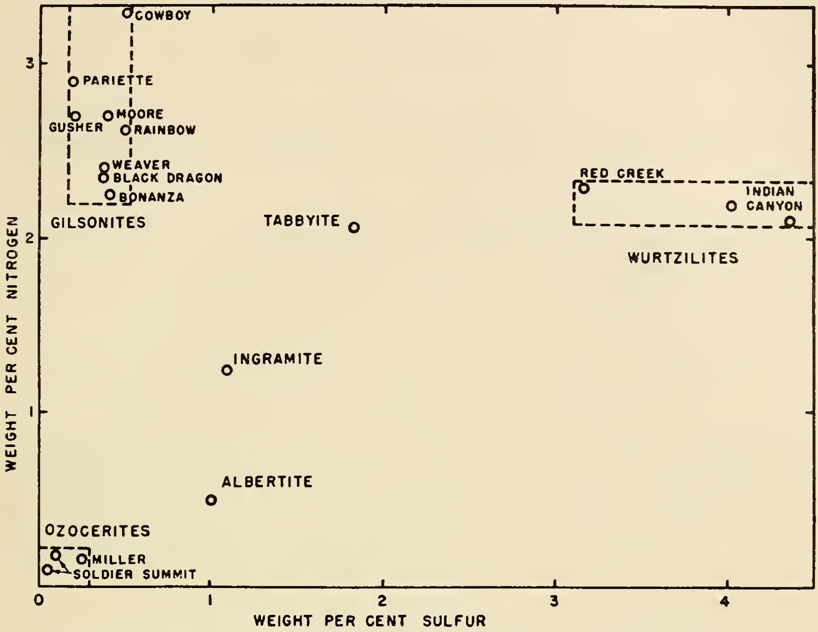

Fig. 8. Sulfur and nitrogen content of the Uinta Basin bitumens.

Only one analysis each was available for tabbyite, ingramite, and albertite, but they seem to fall in between gilsonite and wurtzilite in sulfur content. Gilsonite samples from several different localities are remarkably uniform in elemental composition, all being high in nitrogen (2.25–3.29%) and low in sulfur (0.22–0.53%). The high nitrogen content indicates that proteinaceous material played an important part in the origin of gilsonite. Ozocerites are low in both nitrogen and sulfur.

The mechanism of the oxidation of asphaltic materials can proceed along two paths; (1) the addition of oxygen to form unstable compounds from which water, carbon dioxide, or other unstable oxygen-containing substances are eliminated leaving unsaturated compounds which then polymerize, and (2) the addition of oxygen to form stable oxygenated compounds. Some deductions as to the possible oxidation mechanism for a bitumen such as gilsonite can be made from elemental analyses of the material in various stages of weathering.

Data of this type have been obtained for a group of gilsonites and are shown in Fig. 9. The percentages of elemental constituents for 10 gilsonites are plotted against the percent asphaltenes, which is a rough measure of the extent of polymerization. Inasmuch as asphaltenes are of high molecular weight, an increase in the average molecular weight of the substances occurs with an increase in asphaltenes. Liquid asphalts are low in asphaltenes and the hard solid asphalts are high in asphaltenes; consequently, asphaltenes can be used to measure the change from liquid to semi-solid, to solid which represents various stages of weathering.

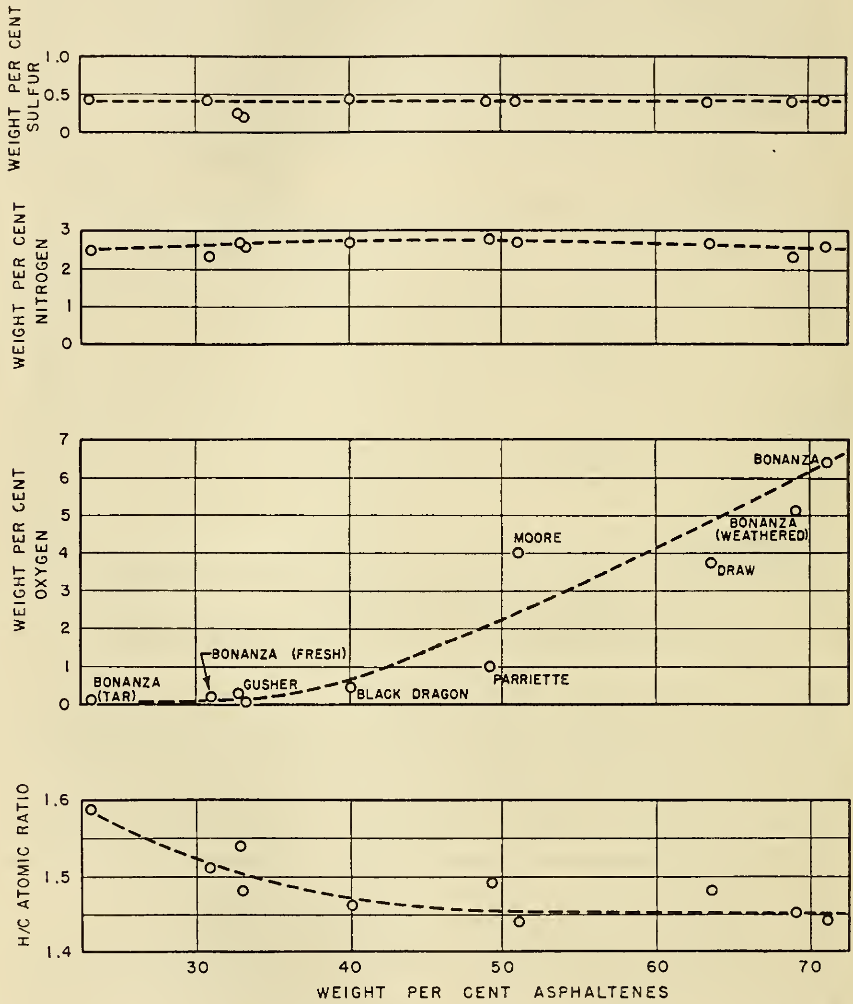

Fig. 9. Relation between elemental constituents and asphaltenes in ten gilsonite samples.

The data in Fig. 9 show a very interesting relationship. In going from Bonanza tar with 23% asphaltenes to some of the fresh samples of solid gilsonite with 30 to 40% asphaltenes *there is no appreciable increase in the oxygen content but there is a definite lowering of the hydrogen to carbon ratio.* This signifies that the change from liquid to solid forms of gilsonite is chiefly a polymerization reaction with loss of hydrogen (probably as water). However, in going from the fresh solid to the more weathered solid forms of gilsonite having from 40–70% asphaltenes, there is little change in the hydrogen to carbon ratio but a definite increase in the oxygen content. This indicates that the alteration of the more weathered forms of gilsonite is a result of the formation of stable oxygenated compounds rather than of increased polymerization. It is also interesting to note that neither the sulfur nor the nitrogen content varies appreciably. Apparently neither of these elements is lost or concentrated in going from the tar to the solid weathered gilsonite.

Separation of hydrocarbons from bitumens by chromatography. The chromatographic procedure involves dissolving the bitumen in some light hydrocarbon, such as n-heptane, and passing it through a column of activated alumina. This is followed by benzene and methanol, ether, or pyridine. The heptane removes the paraffin and naphthene hydrocarbons; the benzene, the aromatic hydrocarbons; and the methanol, the nitrogen, oxygen, and sulfur compounds (non-hydrocarbons). The separations are not quantitative and it usually is necessary to repeat the procedure to obtain an accurate analysis. The approximate distribution of hydrocarbon types in ozocerite and liquid gilsonite by this method is shown in Table 4. The high paraffinicity of ozocerite and the aromaticity of gilsonite are evident from these data. Infrared analyses of the chromatographic fractions also showed that there are paraffin chains in the aromatic, and in the nitrogen, sulfur, and oxygen compounds of ozocerite.

TABLE 4

Chromatographic Separation of Hydrocarbons from Ozocerite and a Liquid Form of Gilsonite

Compound type	Weight percentage in	
	Ozocerite	Liquid gilsonite
Paraffin and naphthene hydrocarbons	81	18
Aromatic hydrocarbons	10	48
Nitrogen, sulfur, and oxygen compounds*	9	34

* May contain some hydrocarbons not eluted by heptane or benzene.

Summary of compositional data. The Uinta Basin bitumens are complex mixtures of high molecular weight hydrocarbons and non-hydrocarbons which can be separated into fractions consisting of an oily medium, asphaltic resins, asphaltenes, and carboids. These groups merge into one another and their atomic H/C ratios decrease with each succeeding member, except for the carboids which differ mainly in having more oxygen than the asphaltenes. The asphaltenes are usually aromatic, the asphaltic resins are aromatic or naphthenic, and the oily medium may be naphthenic or paraffinic in structure. The molecular weights of these groups vary from about 500 for the oily medium and resins to 30,000 for the asphaltenes, and probably higher for the carboids.

The distinct differences in the Uinta Basin bitumens are due to the differences in the structural units forming the constituent groups. Although asphaltenes are usually aromatic, they may have naphthenes in them. Likewise, the oily medium may be more aromatic than naphthenic or paraffinic, and sulfur or nitrogen linkages may be introduced in the units. Sulfur, particularly, can act as a crosslinking agent to impart rigidity and insolubility to the bitumen. A description of the probable structures of the individual Uinta Basin bitumens based on all available data is presented below.

TABLE 5.*

Composition of Ash of

Serial no.	Bitumens	Deposit	Ash, %		
				XX.	X.
247613	Albertite	NE 1/4 sec. 23, T.10S., R.8E. Salt Lake Meridian	0.3		Al, Fe, Mg, Ca, Ni
222075	Gilsonite	Rainbow Vein, Dragon Mine, Green River Fm.	0.3		Al, Fe, Ca, Mg, Na, Co, Ni
211050	Gilsonite	Rainbow Vein, Rainbow Mine, Uinta Fm.	0.1	Na, Ni	Al, Fe, Ca, Co
69276	Gilsonite	Cowboy Vein	0.09	Ni	Si, Fe, Al, Ca, Na, K, Co, Mo
222073	Gilsonite	Wagonhound Vein	0.1	Ni	Al, Fe, Ca, Na, Co, Zn
223230	Gilsonite	Fort Duchesne Vein	0.09	Ni	Al, Fe, Ca, Mg, Co
223228	Ozocerite	Pleasant Valley Mine, NW 1/4 sec. 24, T.11S., R.8E. Salt Lake Meridian	0.1	Na	Ca
223229	Ozocerite	Soldier Summit Mine, NW 1/4 sec. 30, T.10S., R.8E.	0.2	Ca	Al, Fe, Mg
247612	Wurtzilite	Zirker Mine, Indian Canyon	0.06	Na	Al, Mg, Ca, Ti, Ni
247611	Wurtzilite	Lake Canyon	0.05		Al, Mg, Ca, Na, Ti, Ni
96059	Rock Asphalt	Asphalt Ridge	0.49	Al	Fe, Ca, Cu
223235	Asphalt	Sunnyside	0.3	Ca	Al, Fe, Ti, Mg, Na, Ni
96046	Asphalt	PR Springs	0.37	Fe	Al, Ca, Cu, Ni

* Analyses by A. T. Myers, C. A. Horr, N. M. Conklin,

Ozocerite is composed principally of straight and branched chain saturated hydrocarbons with some naphthene groups. The sum of oxygen, nitrogen, and sulfur averages less than 0.5%. The H/C ratio of 1.96 is approximately that of the —CH_2— group. The low refractive index, low carbon residue, and absence of aromatic peaks and presence of a strong paraffinic peak in the infrared spectra identify a predominantly paraffinic material. The presence of ceresin wax crystals under the microscope and the infrared band at 7.6 μ indicate that some branched chain and naphthenic groups are present. The chain length deduced from melting point and X-ray data is in the C_{25}–C_{35} range.

Gilsonite is predominantly aromatic, containing condensed ring aromatic structures in the high molecular weight asphaltene fraction and simpler dinaphthyl structures in the oil constituents and resins. It has few paraffins in the oily constituents. Both nitrogen and oxygen linkages are present,

Bitumens (*Bell*, 1960)

Composition of ash (%) by spectrochemical analysis			
.X	.0X	.00X	.000X
Na, Ti, Mn, Ba, Co, Mo, V	B, Cu, Sr, Zr	Cr, Pb, Y, Yb	Ag
Ti, Mo, Zn	Mn, B, Ba, Cu, Pb, Sr, V, Zr	Cr, Nb, Sn, Y	
Ti, Mg, As, Mo, V, Zn	Mn, B, Ba, Cu, Pb, Sn, Sr, Zr	Cr, Ge	Ag, Yb
Cr, Pb, V, Zn, As, Ti, Sb	Mn, La, B, Ba, Sn, Sr, Tl, Zr	Y, Ag, Bi	Sc
Ti, Mg, As, Cu, Mo, V	Mn, B, Ba, Ge, Pb, Sn, Sr, Y, Zr	Ag, Cr, Nb, Yb	
Ti, Na, As, Mo, Zn	Mn, B, Ba, Cu, Pb, V, Zr	Ag, Cr, Nb, Sn, Sr	
Al, Fe, Mg, Ni	Ti, Mn, Ag, Ba, Cu, Sr, V	Co, Cr, Nb, Pb, Zr	
Ti, Mn, Na, Ba, Ni, Sr, V	B, Cu, Sn, Zr	Co, Cr, Nb, Pb, Y	Ag
Fe, Ba, Co, V	Mn, B, Cr, Cu, Mo, Pb, Sr, Zr	Ga	Ag
Fe, B, Ba, Co, Mo, V	Mn, Cr, Cu, Pb, Sr, Zr		Ag
Mg, Na, B, Ni, Zn	Ti, Mn, Ba, Co, Cr, Pb, Sc, V, Zr	Ag, Mo, Y, Yb	Be
Mn, Ce, Co, Cu, La, Mo, V, Nb, Nd, Zn	B, Ba, Cr, Pb, Sc, Sn, Sr, Y, Zr	Be, Yb	Ag
Mg, Na, Ti, Mn, B, La, Ce, Nd, Zn	Co, Cr, Mo, Pb, Sc, Sr, V, Y, Zr	Ag, Ba, Nb, Yb	

P. J. Dunton, D. L. Ferguson and R. G. Havens.

particularly in the higher molecular weight fractions, but the sulfur content is low. Some carbonyl and other oxygenated compounds are present in the oily constituents and resins. Over 50% of the solid gilsonite probably consists of non-hydrocarbons.

The high carbon residue and refractive index indicate that condensed rings are present. The low atomic H/C ratio of 1.42 establishes the aromatic character of gilsonite. Infrared spectra show the presence of *para* and *meta* substituted aromatics and oxygenated compounds, and the absence of long paraffin chain structures. The elemental analysis shows that gilsonite is high in oxygen and has the highest nitrogen content of the Uinta Basin bitumens. The solubility of gilsonite in CS_2 establishes that it is not purely a condensed ring system.

Wurtzilite is naphthenic in character with naphthene rings rather than aromatic rings predominating in the higher molecular weight fractions. Chains of five or more $—CH_2—$ groups are attached to the naphthene units in both the oily constituents and the asphaltenes. Wurtzilite contains some oxygen, probably in the form of carbonyl side chains and oxygen bridges. It also has a high sulfur content (4%). The low carbon residue and refractive index, and the high atomic H/C ratio of 1.60 definitely establish that wurtzilite has very few condensed ring aromatics in its structure. The absence of strong infrared peaks in the aromatic region at 11.5 and 12.3 μ further substantiates this conclusion. Its infusibility and insolubility probably arise from the joining of multiple units of naphthene rings with sulfur and oxygen acting as crosslinking units. The presence of strong infrared absorption peaks due to paraffin chains, $>C=O$, and other oxygen linkages establishes that these groups are present in wurtzilite.

Albertite is composed predominantly of condensed aromatic ring structures with the oily constituents containing polycyclic aromatics, carbonyl groups, and some paraffin chains. It has less sulfur and nitrogen than any other Uinta Basin bitumen except ozocerite.

The very high carbon residue, high refractive index, and low atomic H/C ratio establish the presence of the condensed aromatic rings. The insolubility and infusibility of albertite indicate the condensed rings to be of several more units than in gilsonite. The infrared spectra of the oily constituents and asphaltenes establish the presence of carbonyl groups, polycyclic aromatics, and some paraffin chains.

Ingramite appears to be a less polymerized form of albertite. The oily constituents and asphaltenes of ingramite have the same infrared spectra as those of the soluble fraction of albertite, but ingramite has a higher atomic H/C ratio and lower carbon residue than albertite. These properties would be characteristic of a less polymerized form.

Tabbyite has an infrared spectrum similar to gilsonite except that weaker infrared peaks in the carbon–oxygen regions indicate that fewer oxygenated compounds are present in tabbyite. In all other properties, such as refractive index, sulfur content, and atomic H/C ratio, it resembles wurtzilite. It is probably some intermediate type of bitumen.

Trace metals in Uinta Basin bitumens—The ash content of Uinta Basin bitumens ranges from a trace up to a few tenths of 1%. The greater part of this ash probably represents metallic elements that are constituents of organic compounds rather than included rock particles, clay, and other sedimentary detritus. Table 5 shows the trace metal content of several samples of bitumens as determined by semi-quantitative spectrochemical analysis. A dry ashing procedure was used to eliminate organic matter. Perhaps the most significant features indicated by the data are the rather high nickel contents and the comparatively low vanadium contents of these bitumens.

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Chapter 9

GEOCHEMISTRY OF ORGANIC PIGMENTS

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Porphyrins

Introduction—Porphyrins form the basic structural units of respiratory catalysts throughout the plant and animal kingdoms. Chlorophyll, the green pigment of plants, is the agent of photosynthesis and allows the fixation of solar energy in the form of carbohydrates and other food materials. Furthermore, it appears that photosynthesis or related processes indirectly account for the fixation of solar energy in the form of petroleum and bituminous substances—the fossil fuels that supply much of the energy on which our civilization depends. Hemoglobin, the red pigment of blood, is the respiratory pigment of high animals; transporting oxygen and waste products it allows their efficient operation. A third series of pigments, less understood but closely related to hemoglobin, is comprised of enzymes such as the cytochromes that participate in the regulation of cellular respiration. Present-day civilization, therefore, depends on hemoglobin-type pigments for life processes and on chlorophyll-type pigments for energy sources.

The activities of the respiratory pigments are accounted for in part by the metals with which they are complexed. Iron is characteristic of the respiratory pigments of animals, and magnesium is the metal involved in the basic plant process, photosynthesis.

The structures of the "life" pigments are quite similar. Hemoglobin is comprised of heme, a porphyrin complexed with ferrous iron, and globin, a slightly basic, water-soluble protein. Enzymes of the cytochrome system contain the same type of "heme" as hemoglobin, combined with different proteins. Chlorophyll contains a chlorin (a porphyrin in which one double bond of a pyrrole group has been saturated by the addition of two hydrogen atoms) complexed with magnesium and having a phytol alcohol group ($C_{20}H_{39}OH$) instead of a protein group. The structures of chlorophyll and hemin are shown in Fig. 1.

Proof of structure of these pigments and the chemistry of their porphyrin constituents resulted from the extensive efforts of many workers notable among whom were W. Kuster, R. Willstätter, and Hans Fischer. Hoppe-Seyler (1871) prepared the first porphyrin, originally named the class, and showed the relationship of chlorophyll to hemoglobin by obtaining a porphyrin in the degradation of chlorophyll and a similar product by the action of concentrated sulfuric acid on hemoglobin. The work of Fischer (1929) in establishing the cyclic nature of the porphyrin ring and in synthesizing hemin remains an unparalleled classic in structural chemistry.

Although most of this early work was published in the German language, including the basic porphyrin references by Fischer and Orth (1937) and Fischer and Stern (1940) and the early chlorophyll reference by Willstätter and Stoll (1913), several modern reference works present authoritative reviews of the early work together with recent advances. Foremost among these are the work of Rabinowitch on photosynthesis and chlorophyll (1945, 1951), the monumental volume of Lemberg and Legge (1949) containing 3182 references, the works of Vannotti (1954) and Mayer and Cook (1943), and the reviews of Corwin (1943), Steele (1943), Armstrong (1933) and Aronoff (1950). An exhaustive treatment of the chemistry of porphyrins and the pigments from which they are derived is beyond the scope of the chapter. The reader is referred to the above references for details on which this general discussion is based. Where the original sources commonly are not available, reference will be made to the reviews of such work.

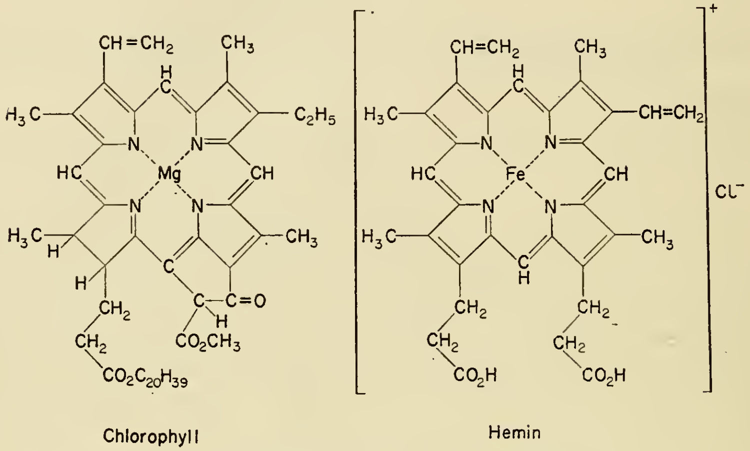


FIG. 1. Structures of hemin and chlorophyll.

A brief comparison of the degradation products of chlorophyll and hemoglobin will emphasize the relationships of the various derivatives. Removal of the protein, globin, from hemoglobin results in *heme*, a porphyrin complexed with ferrous iron. Ferric porphyrin complexes in which one of the valences is satisfied by an hydroxyl group are known as *hematins*. Ferric porphyrin complexes associated with some negatively charged group such as the chloride ion are known as *hemins*. According to the nomenclature of Lemberg and Legge (1949), the general name for an iron–porphyrin complex is *hematin*. Removal of iron from a heme, hemin, or hematin results in a *porphyrin*.

The derivatives of chlorophyll are more numerous and are conspicuous for their unsystematic nomenclature. The common usage, however, probably is preferable to the extremely long systematic names that would be appropriate. The situation is further complicated by the existence of several chlorophylls. The two common forms are chlorophyll *a*, shown in Fig. 1, and chlorophyll *b* which differs from chlorophyll *a* in containing an oxygen atom in place of two hydrogen atoms. A less common pigment, bacteriochlorophyll, differs from chlorophyll *a* in that it contains an acetyl group in place of one of the vinyl groups, and two additional hydrogen atoms. This substance, the photosynthetic pigment of purple and brown bacteria, has been discussed by Rabinowitch (1945, p. 444; 1951, p. 617). It should prove of considerable geochemical interest because it is characteristic of primitive organisms and is considered by Lemberg and Legge (1949, p. 650) to be an evolutionary precursor of chlorophyll.

Chlorophyll *a* will be used as an example of the degradation of the chlorophylls according to the treatise of Willstätter and Stoll (1913). Chlorophyll, on treatment with alkali, loses the phytol group to form a *phyllin*, corresponding to a hematin in the animal series. Phyllins readily lose the magnesium atom under acidic conditions to form *chlorins* or *porphyrins*, depending on the reaction conditions. Chlorins are *dihydroporphyrins*, containing one less double bond in one pyrrole nucleus. Products analogous to the chlorins, produced from chlorophyll *b*, are called *rhodins* and still contain the extra oxygen atom. The corresponding products from bacteriochlorophyll are called *bacteriochlorins* and are tetrahydroporphyrins.

Because the magnesium of chlorophyll is very labile, a different route of degradation, discussed by Steele (1943), often occurs. The loss of magnesium from chlorophyll produces a *pheophytin*. This, in strong acids, loses the phytol group to form a *pheophorbide*. A pheophorbide upon alkaline saponification reacts to form a *chlorin*. Thus, the same product, chlorin, may be prepared in two ways. Chlorin, under drastic alkaline degradation, forms the dicarboxylic acid, *rhodoporphyrin*, and the monocarboxylic acids, *phylloporphyrin* and *pyrroporphyrin*. Pheophorbides, under mild reducing conditions, react to form phylloerythrin, and upon further reduction, *desoxophylloerythrin*, which retain the isocyclic ring of chlorophyll. Phylloerythrin may also be formed by refluxing various of the chlorophyll intermediates discussed above in strong acid. The porphyrins derived from chlorophyll may be decarboxylated to form the common pyrro- and phyllo-etioporphyrins which correspond to mesoetioporphyrin of the animal pigments. Essentially then, the corresponding derivatives of chlorophyll and hemoglobin are the phyllins and hematins, the chlorins which have one double bond less than the porphyrins, and the erythrins which have an isocyclic ring in conjunction with the porphyrin nucleus.

Composition and types—Porphyrins existing naturally in a free state or complexed with various metals may be considered to be derivatives of the cyclic ring system represented by the porphyrin nucleus, sometimes called *porphin* or *porphine.* This compound is comprised of four pyrrole rings linked together to form the highly conjugated molecule shown in Fig. 2. The large number of conjugated double bonds, together with the heterocyclic nitrogen groups and consequent high degree of aromatic stabilization, account for the unusual stability of the molecule and the strong color common to the porphyrins. The pyrrole pigments are highly stabilized and deeply colored biological compounds; they absorb light strongly at intervals throughout the visible spectrum and far into the ultraviolet and infrared. The resonance of the respiratory pigments is of fundamental importance in their action as discussed by Lemberg and Legge (1949). This resonance causes them to be so stable as to permit the existence of free radicals in aqueous media, a property that in conjunction with the varying valence of iron allows the animal pigments to act as respiratory catalysts. Resonance probably accounts also for the action of chlorophyll in photosynthesis.

The structures of the several porphyrin species from hemoglobin may

TABLE 1.
Composition of Typical Porphyrins

Porphyrin	Substituents of pyrrole nuclei				Other groups
	Hydrogen	Methyl	Ethyl	Propionic acid	
Porphyrin (porphin)	8	—	—	—	—
Pyrroetioporphyrin	1	4	3	—	—
Phylloetioporphyrin	1	4	3	—	1—CH_3 on Meth. Bridge
Mesoetioporphyrin	—	4	4	—	—
Pyrroporphyrin	1	4	2	1	—
Phylloporphyrin	1	4	2	1	1—CH_3 on Meth. Bridge
Rhodoporphyrin	—	4	2	1	1—CO_2H
Deuteroporphyrin	2	4	—	2	—
Mesoporphyrin	—	4	2	2	—
Protoporphyrin	—	4	—	2	2—$CH{=}CH_2$ (Vinyl)
Hematoporphyrin	—	4	—	2	2—$CHOHCH_3$
Coproporphyrin	—	4	—	4	—
Uroporphyrin	—	—	—	4	4—CH_2CO_2H
Desoxophylloerythrin	—	4	2	1	Isocyclic Ring (Methene)
Phylloerythrin	—	4	2	1	Isocyclic Ring (Carbonyl)
Pheoporphyrin	—	4	2	1	Isocyclic Ring (Carboxylic and Carbonyl)
Porphyrin Derivatives:					
Chlorin	3	4	2	1	—
Rhodin	2	4	2	1	1—CO_2H
Bacteriochlorin	5	4	2	1	—

be shown by substituting various side chains for the eight outer hydrogen atoms of the four pyrrole nuclei. The prototype for animal porphyrins is mesoporphyrin IX, $C_{20}H_6N_4(CH_3)_4(C_2H_5)_2(CH_2CH_2CO_2H)_2$, which has the structure shown in Fig. 3. This compound presently is prepared by the method of Corwin and Erdman (1946), which involves the one-step reduction of the vinyl groups and removal of iron through the action of formic acid and colloidal palladium on hemin. Each porphyrin is capable of having several isomers which differ only in the arrangement of their side-chains. The possibility of electronic isomers, depending on the location of the hydrogen atoms on the central nitrogens, is discussed by Corwin (1943) who concludes that the problem is not capable of resolution on the basis of available data. The porphyrins found in nature have either alternating arrangement of side chains or asymmetrical arrangement; the latter are far more common. There are fifteen possible spatial isomers of mesoporphyrin. The Roman numeral IX indicates the type of substitution found in natural mesoporphyrin shown in Fig. 3. Lemberg and Legge (1949, p. 55) report that the various porphyrins derived from hemoglobin or natural hematin compounds all are of type IX. The natural etioporphyrin, etioporphyrin III or mesoetioporphyrin, is formed if the two propionic acid groups are decarboxylated to form ethyl groups.

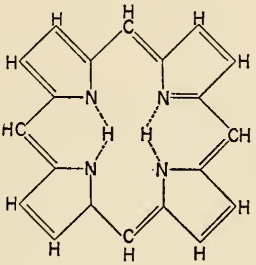


FIG. 2. Structure of porphyrin nucleus.

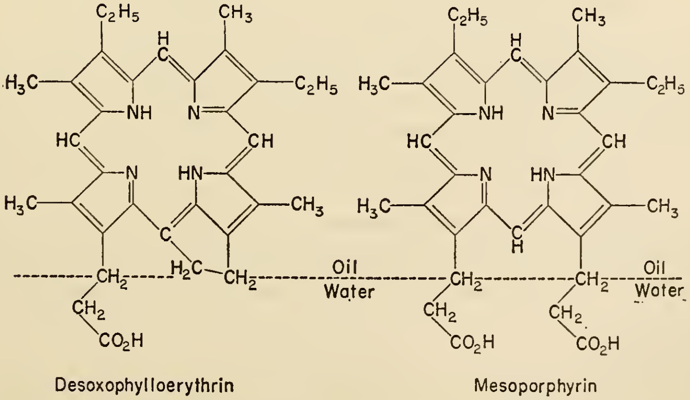
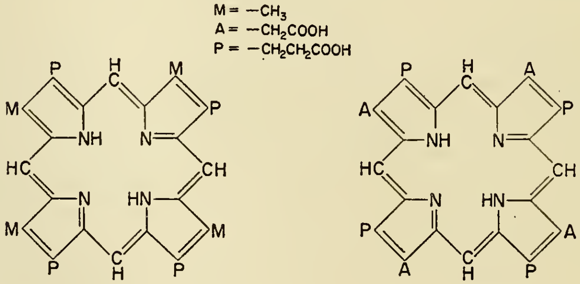


FIG. 3. Structures of typical porphyrins and orientation at the oil–water interface.

For geochemical purposes, the prototype of plant porphyrins is desoxophylloerythrin. The structure of this chlorophyll derivative is shown in Fig. 3. The side chain arrangement here is of the same type (asymmetrical) as that of mesoporphyrin IX except that one of the propionic acid groups forms an isocyclic ring. Phylloerythrin, another plant product, contains a carbonyl group in place of the CH_2 group in the isocyclic ring next to the pyrrole ring. The other important plant porphyrins also have the side-chain arrangement indicated by type IX.

The constituent groups which, coupled with the porphyrin nucleus, constitute the various common plant and animal porphyrin materials are summarized in Table 1, according to data primarily from Lemberg and Legge (1949).

Occurrence—The almost universal distribution of pyrrole pigments, in the most advanced as well as in primitive organisms, is reviewed by Lemberg and Legge (1949). Uroporphyrin (Fig. 4) is excreted in large quantities by humans having a pathological condition known as porphyria; the zinc complex of this porphyrin also has been identified in the urine of such patients. Deuteroporphyrin also is found in faeces as a product of the action of intestinal bacteria on blood pigments. Small quantities of protoporphyrin normally are found in the red corpuscles of man, in larger quantities in lead poisoning or anemia where it is found in the bone marrow. Coproporphyrin (Fig. 4) normally is eliminated in low concentrations in the urine and is present also in milk and faeces. The production of porphyrins by tubercule and diphtheria bacilli has been extensively studied. Vannotti (1954, p. 46) reports that there exist in diphtheria bacillus cultures complex porphyrin salts of iron, copper, and zinc. For these reasons, porphyrins have been studied extensively by clinical scientists and much of the chemistry of porphyrins has been developed in such investigations. The application of these established principles for geochemical purposes, however, is a relatively new and rapidly expanding field of research.



Coproporphyrin III

Uroporphyrin I

FIG. 4. Structures of porphyrins excreted by animals.

Various microorganisms are capable of forming porphyrin compounds. For example, bacterioviridin, the pigment of green bacteria, apparently is an intermediate between chlorophyll *a* and bacteriochlorophyll; it contains an acetyl group in place of the vinyl group of chlorophyll but has the same chlorin nucleus. Mayer and Cook (1943, p. 315) report that the pigment of purple bacteria is a porphyrin very similar to oxypheoporphyrin.

The synthesis of porphyrins by yeast has been studied systematically by Fischer and associates (1924; 1937, p. 50). These investigators observed the simultaneous formation of coproporphyrin, hemin, and cytochrome in yeast cultures. Yeasts are widespread and form durable spores. Furthermore, they probably are of as early an origin as bacteria and evidence of budding fungi in the fossilized remains of plants from the Devonian age has been reported. The synthesis of "animal-type" porphyrins by yeasts and in the root nodules of leguminous plants, reported by Lemberg and Legge (1949), is of considerable geochemical interest as discussed below.

According to the works of Lemberg and Legge (1949) and Vannotti (1954), porphyrins are found in the bones of wild and domesticated animals, in the Harderian glands of rodents, in the spines of hedgehogs, egg shells, feathers and bones of various fowls, the red streak of the earthworm, shells of certain molluscs, and in corals and sea anemones. Hemoglobins of various types also are widely spread. Erythrocruorin (red invertebrate hemoglobin with a different protein) is found in nematodes, annelids, crustaceans, insects, molluscs, and echinoderms. Chlorocruorin, the green blood-pigment of certain polychetes and having a vinyl group of heme replaced by a formyl group, is found in the plasma of several marine worms.

Lemberg and Legge (1949) also report that the cytochromes are widely distributed in animal tissues of practically every type, being especially rich in heart tissue. Moreover, the cytochromes are found in germinating seeds and many other plant cells, and also appear in baker's yeast and in many bacteria. In fact, Lemberg and Legge (1949) report that it is only in anaerobic types that the cytochromes are not identified. However, with the exception of cytochrome *c*, the cytochromes actually are spectroscopically observed rather than definitely established substances.

The chlorophylls are distributed throughout the Plant Kingdom and, in addition, several pigments similar to chlorophyll apparently are produced in nature. One interesting example is bacteriochlorophyll, the photosynthetic pigment of purple and brown bacteria. Another, protochlorophyll, is a green pigment found in seed cases and apparently differs from chlorophyll in having an additional vinyl group.

Properties—*Spectra.* The most distinctive property of the porphyrins is their absorption of light resulting in spectra which generally consist of four strong absorption bands in the visible region. The locations of these peaks vary somewhat with type of porphyrin and solvent, but generally are located at about 620, 565, 535, and 500 mμ, and are labeled I through IV, respectively. In addition, porphyrins have a very strong band at about 400 mμ which is known as the Soret band. These peaks cause the porphyrin solutions to have a typical red-violet color and make easy and definite recognition possible with a simple spectroscope.

Specific properties of the organic solvents commonly used cause slight shifts in the peak locations and intensities of a given porphyrin. A typical example is shown in Fig. 5. This figure also shows the presence of a small peak (Ia) at about 590 mμ which is observed with pure samples in dioxane solution. Another solvent effect is that this peak is repressed by chloroform to such an extent that it often is indistinguishable.

Solvent effects on the spectra of animal porphyrins have been discussed by Lemberg and Legge (1949, p. 73). The visible spectra of porphyrins in weakly basic solutions resemble those obtained in organic solvents although the Soret peak is weakened and shifted about 20 mμ toward shorter wave lengths. These changes are small because of the separation of the carboxylic acid groups from the porphyrin nucleus by aliphatic groups. In acidic solutions, the visible absorption spectrum is changed markedly by cation formation resulting in two peaks, a major peak at about 550 mμ and a minor one at about 595 mμ. The Soret peak remains at about the same position but may be weakened by strong acids.

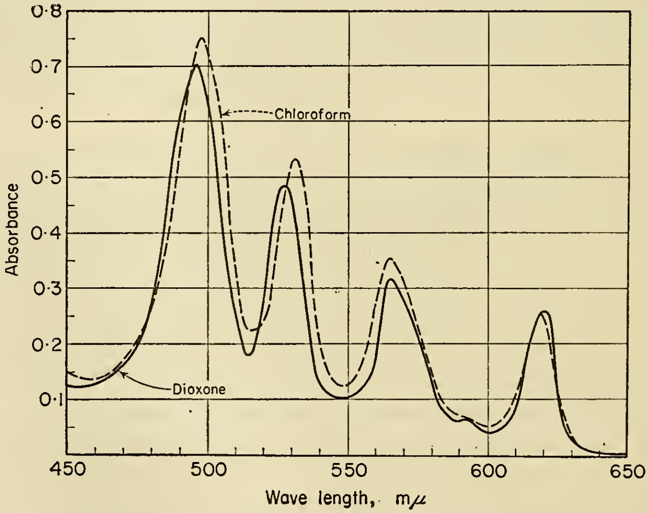


FIG. 5. Absorption spectra of mesoporphyrin IX dimethylester (concentration 6.15×10^{-5}M).

The spectra of porphyrins in neutral organic solvents or in acidic solutions are typical and fundamental for the recognition of porphyrins in general. Spectrophotometers of the Beckman DU or DK types commonly are used for quantitative measurements. The Hartridge reversion spectroscope is particularly useful for establishing the exact positions of absorption peaks because it can be read directly to tenths of a millimicron. It may, however, give slightly erroneous readings for unsymmetrical peaks unless the solutions are diluted carefully. Despite their general usefulness, too much weight should not be given to spectral studies alone. Often two porphyrins of considerably different structures exhibit nearly identical spectra. The absorption spectra of some typical porphyrins are summarized in Table 2.

TABLE 2.
Absorption Spectra of Porphyrins in the Visible Region
Dioxane solutions, Falk and Willis (1951)

Porphyrin	Absorption Maxima mμ				Relative Intensity			
	I	II	III	IV	I	II	III	IV
Etioporphyrin I	621	567	528	496	0.390	0.462	0.712	1.0
Deuteroporphyrin dimethyl ester	618	565	525	495	0.274	0.430	0.536	1.0
Mesoporphyrin IX	620	567	528	496	0.376	0.459	0.690	1.0
Protoporphyrin dimethyl ester	630	575	537	502	0.380	0.461	0.793	1.0
Rhodoporphyrin	632	573	545	506	0.184	0.699	1.270	1.0

Although the spectra of porphyrins in weakly basic solutions are similar to those in neutral solvents, in strongly basic environments the central nitrogen atoms form disalts which are analogous to the dihydrochlorides formed in hydrochloric acid. According to the data of Erdman and Corwin (1946), the disodium salt and dihydrochloride of etioporphyrin have very similar spectra with peaks at 590, 555, and 418 mμ, and at 590, 555, and 415 mμ, respectively, in dioxane solutions. These workers concluded that the shift in charge and presence or absence of hydrogens were of slight importance to the bond distribution of these forms. The copper complex had a similar spectrum with peaks at 565, 525, and 395 mμ, except that the order of intensity of the visible peaks was reversed. The spectrum of the neutral porphyrin is markedly different, having four peaks in the visible region as discussed above. Erdman (1946) interpreted these results as indicating a very different bond distribution, in the free porphyrin, as would result from destroying the equivalence of the nitrogen atoms through unique hydrogen placement. These results were theoretically correlated. Analysis of the energy components of the porphyrin molecule indicates that the Soret peak (about 400 mμ) is a half-ring energy function, essentially a dipyrrylmethene band. Consideration of the wave functions for the whole porphyrin ring indicates that there are four positions above ground state. These wave functions have different values and four bands result from twofold symmetry. For fourfold or higher symmetry, two each of the wave functions assume equal energy resulting in two bands in the visible region. This is the case for the disodium salt, dihydrochloride, and complex of a divalent transition metal such as copper. Erdman and

Corwin (1946) observed that N-methyletioporphyrin had a spectrum similar to that of the neutral porphyrin. Since the former has twofold symmetry, these results confirmed their deduction that hydrogen bonding in the neutral porphyrin could not extend to the point of "sharing".

Rabinowitch (1951) concluded that the four peaks of the neutral porphyrin spectrum represent vibrational fine structure of a single electronic transition and that the Soret peak represents a separate electronic transition.

Variations in the intensities of the four visible bands are due to perturbations caused by substitutions on the periphery of the ring and apparently are largely a symmetry effect. Attempts to correlate the types of spectra that result from such substitution have been largely empirical and often misleading. However, some types of spectra, which vary in the relative intensities of the four visible peaks, are so typical that they have been distinguished by specific names. Diagrams of these types appear in the works of Fischer and Orth (1937), Aronoff (1950) and Rabinowitch (1951). The three common types of neutral porphyrin spectra are designated as the 'etio', 'phyllo', and 'rhodo' types which are reproduced in Fig. 6.

As observed in Fig. 6, the intensities of the peaks of the etio-type spectra increase regularly proceeding from peak I to IV. This spectrum also has a small peak (Ia) between peaks I and II. Despite some references to this effect, this peak may not be limited to the etio spectrum and may appear in other spectra. In the phyllo spectrum, peak III is not as strong as peak II. The nomenclature is unfortunate because the "etio" term does not necessarily indicate decarboxylation as it does elsewhere in porphyrin work. For example, mesoporphyrin IX exhibits the etio spectrum (Fig. 5). While the phyllo spectrum usually denotes porphyrins of plant origin and the etio spectrum an animal source, pyrroporphyrin (a plant product discussed above) has the etio spectrum. Among the natural porphyrins, the phyllo spectrum indicates a porphyrin having a substituent on one of the four methene carbon groups, commonly a part or residue of the isocyclic ring, or "adjacent" rather than opposite substitution. Thus pyrroporphyrin, which contains no residue of the isocyclic ring, has the etio spectrum and the spectral properties of pigments of the mesoporphyrin type. For geochemical correlations of spectral properties, it may be concluded that porphyrins derived from bituminous substances and having the phyllo spectrum probably are derived from the chlorophyll series. Porphyrins having the etio spectrum may be from the hemoglobin series but also may be of plant origin. Porphyrins characterized by etio and phyllo spectra first were isolated from crude oil and other bituminous substances by Treibs (1934a, 1934b, 1935a, 1935b, 1936). However, porphyrins having a phyllo spectrum are far more common in petroleum than those having the etio spectrum. Porphyrins having the rhodo spectrum have not yet been isolated from bituminous substances.

The resonance of the porphyrin ring is altered radically when one of the pyrrole groups is hydrogenated. This change is reflected in a sharp change

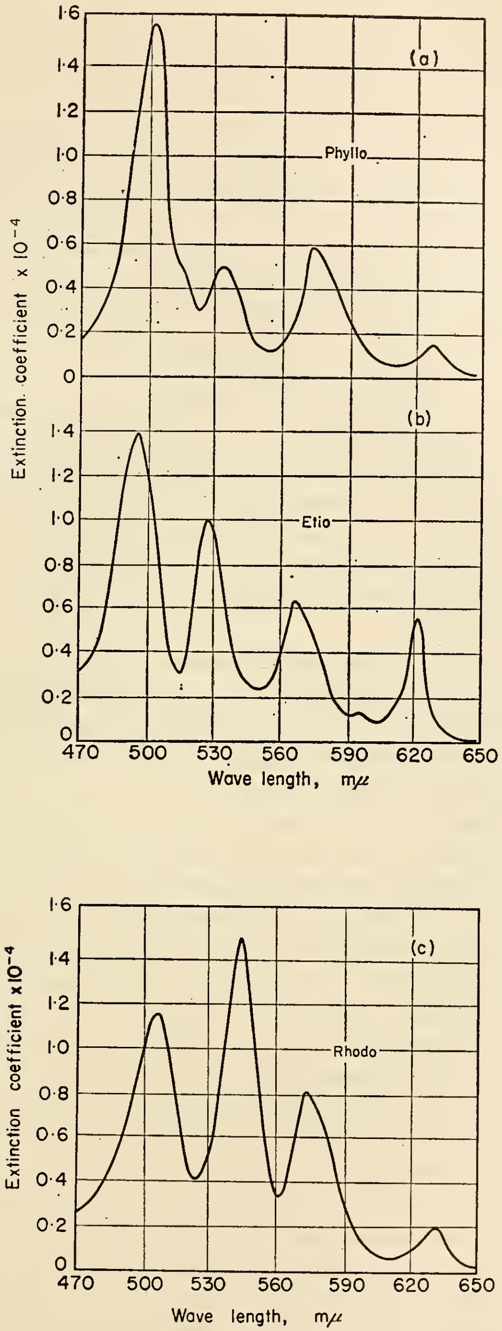


FIG. 6. Types of porphyrin spectra (Fischer and Orth, 1937).

in the appearance of the spectrum accompanying a transition from the porphyrin system to a dihydroporphyrin system typical of the chlorins and rhodins. The theoretical aspects of porphyrin spectra have been discussed by Rabinowitch (1951, p. 622). In the chlorin system, the peaks in the green and yellow are drastically reduced and an intense band appears in the red at about 660 mμ. This band is much more intense than the other visible bands and is about equal to the Soret band. This change in light absorption results in transmission in the green—hence the green color of chlorins and other pigments having this basic structure. The rhodins (chlorins from chlorophyll *b*) do not exhibit such a large change in absorbance properties, perhaps because of the additional methoxy group which they contain.

Seely (1957) has recently made an extensive theoretical study of the spectra of porphyrins and various reduction products including the chlorins. The decrease in intensity of the middle bands and the appearance of a strong band in the red observed in changing from porphyrins to chlorins is paralleled by spectral differences between zinc complexes of the porphyrins and chlorins. This paper also includes a review of much of the spectral work on these substances, correlating their structures and spectral properties.

If a second pyrrole group of the porphyrin nucleus is hydrogenated, as in bacteriochlorophyll and its derivatives, another sharp change in spectral properties is observed. It appears that the red band of the chlorins is shifted to shorter wavelengths (appearing in the orange) while a new, intense band appears in the near infrared.

The infrared spectra of the porphyrins have not been as extensively studied as their visible spectra, primarily because of the ease and simplicity of determining the visible spectra. Furthermore, the visible spectra suffice for rapid recognition of porphyrins in general for quantitative and, with limitations, for qualitative analyses. However, these data are not satisfactory for delineating position isomers and for some other studies of the detailed structures of these substances.

Infrared spectroscopy provides a valuable means of identifying and characterizing the porphyrins and often is useful for distinguishing between closely related isomers. The infrared spectra of several porphyrins and hematins have been determined by Falk and Willis (1951) who were able to obtain definite differences between the spectra of the position isomers coproporphyrin I and III, as observed earlier by Gray and associates (1950). Furthermore, characteristic absorption frequencies of the carbonyl groups in different environments were observed. Falk and Willis (1951) also were able to detect differences in the N–H stretching frequencies between the porphyrins and pyrroles. This was interpreted to indicate that the N–H groups exhibit partial "sharing" of the hydrogen between two of the central nitrogen atoms. This work and the earlier work of Vestling and Downing (1939) showed that the formation of a hematin removed this characteristic band. An absorption peak at about 5.8 μ was observed to be characteristic of a carbonyl group insulated from the porphyrin nucleus. This assignment was used by Dunning and associates (1954) in studies of the selective adsorption of carboxylated porphyrins at an oil–water interface. Falk and Willis (1951) also showed that it was possible to differentiate between a free carboxylic acid group and an ester by infrared measurements. Infrared spectroscopy is a promising tool for the clarification of some of the small but important differences between various porphyrins.

The strong fluorescence of porphyrins under ultraviolet light is another property of importance for their analyses. Porphyrins typically have a strong fluorescence band at about 625 mμ and weaker bands at other wave lengths. The "red" band may be located easily with the Hartridge reversion spectroscope, but location of the other bands requires more extensive equipment. This strong red fluorescence permits the detection of porphyrins at concentrations far below those detectable by absorbance studies and is a valuable tool for this purpose. However, the stable metal-porphyrin complexes found in bituminous materials do not fluoresce. Blumer (1956) recently made an ingenious use of the lack of fluorescence of the vanadium–porphyrin complex for its identification in very small amounts.

Much of the work on porphyrin fluorescence was conducted by Dhere (1937) and by Stern and associates (1937) about twenty years ago and has been reviewed recently by Vannotti (1954). These results show that pure porphyrins may be detected at concentrations of a few parts per billion. The fluorescence spectra of porphyrins have been divided into types I and II, in neutral solvents and in mineral acids, respectively. In neutral organic solvents the main fluorescence band almost coincides with absorption band I, and three weaker bands occur further toward the infrared. In mineral acids the main fluorescence band is at about 600 mμ, corresponding to the first absorption band in acid solutions. The influence of side chains on the position of the emission bands is similar to that on the absorbance bands. Therefore, fluorescence measurements were used by Dunning and Carlton (1956) to supplement absorption data as well as for the detection of minute amounts of porphyrin material.

The observation that the fluorescence of a given porphyrin varies with the pH of the solvent and reaches a minimum at a given pH value, characteristic of the specific porphyrin, forms the basis of a method of identification discussed by Vannotti (1954, p. 23). The method, although excellent in some applications, is limited by the low solubility of many porphyrins in aqueous solutions at or near their isoelectric (neutral) points. Such limitations, and instruments such as the infrared spectroscope which may supply the same and more elaborate information, probably account for the paucity of recent fluorescence studies.

Solubility and partition. Porphyrins are amphoteric compounds having isoelectric points at pH values from 3 to 5. Their acidic characteristics are caused by carboxylated side chains while the two tertiary nitrogens of their nuclei lend them a weakly basic character. The structures of two typical porphyrins are shown above (Fig. 3). The partition of porphyrins between organic solvents and water depends on the hydrophobic nature of the ring and the hydrophilic nature of the central nitrogens and the polar side chains.

The extraction of porphyrins from ethyl ether by acids is an important property for their purification. Willstätter and associates (1913, 1928) observed that different porphyrins require hydrochloric acid of different concentrations for extraction from ether. The "HCl number", which he defined, is the percentage concentration of hydrochloric acid which extracts two-thirds of the porphyrin material from an equal volume of ether. Lemberg and Legge (1949) report that porphyrins with no acidic side chains are extracted from ether only by very strong hydrochloric acid, which forms dihydrochlorides. Porphyrins with two to four carboxylic acid groups are extracted from ether at a pH of 3–4 and porphyrins with 8 carboxylic acid groups cannot be extracted by ether unless the acidic groups are esterfied. The HCl numbers of typical porphyrins are listed by Lemberg and Legge (1949).

The distribution of porphyrins between ether and HCl solutions was made the basis of a procedure known as "countercurrent distribution" by Gregory and Craig (1951). The method was used by Granick and Bogorad (1953) for the separation of deutero- and meso-porphyrins which differ very little in "HCl number". Granick and Bogorad (1953) report that the method is successful for a complete separation of these two similar porphyrins. In this method, about a hundred tubes are arranged in series. Each of these contains acid and ether, between which the porphyrins are distributed. The effect of the progressive transfers of this instrument is to cause the ether phase to move over the lower stationary phase, a dilute HCl solution. The porphyrin with the greater affinity for ether will progress more rapidly so that, if there is enough difference between the porphyrins, they will appear as discrete concentrations bands, much as in a chromatographic column. This method offers a very delicate application of the gross method developed by Willstätter (1913) and used by most workers to establish HCl numbers for porphyrins and for the separation of porphyrins that are quite different. The common HCl extraction method has been most useful in clinical or other work where the porphyrins have major differences. However, Dunning and Carlton (1956) showed that in bituminous materials much of the porphyrin is decarboxylated and the common carboxylated form contains one carboxylic group. Furthermore, because of their strong film-forming tendencies, a considerable amount of the porphyrin aggregate is lost in each extraction, part of it being denatured. Therefore, the common partition method is limited in its applicability for resolving the porphyrin aggregates of petroleum. The more delicate and quantitative method of "countercurrent distribution" may prove very useful for the separation of the more closely related porphyrin types found in bituminous materials.

Paper partition chromatography has proved to be a rapid, effective method for resolving naturally occurring mixtures of porphyrins. Detailed procedures and results are described in the works of Chu *et al.* (1951), McSwiney *et al.* (1949), Nicholas and Rimington (1949), and Rappoport and associates (1955). However, this method has been used primarily for the separation of carboxylated porphyrins and their esters which are of clinical importance, and is new to the petroleum industry.

Paper chromatographic methods for use with porphyrins from bituminous materials were developed by Blumer (1956) and Dunning and Carlton (1956). In studies of pure porphyrins of the type that exist in bitumens, Blumer (1956) observed that decarboxylated, carboxylated, and esterified porphyrins, as well as the metal complexes of these porphyrins, could be separated by two-dimensional paper-sheet methods. The R_f (rate of spot movement relative to rate of front movement) values of the porphyrins were capable of direct correlation with their structures. Blumer (1956) reported that the high R_f values of decarboxylated porphyrins (with a carbon tetrachloride and isooctane solvent) were reduced practically to zero when one or more carboxyl groups were introduced. The R_f values of the esters were considerably higher than those of the porphyrins containing carboxylic groups. Blumer (1956) observed that the formation of complexes with nickel resulted in higher R_f values, as a result of loss of two polar N–H groups. Vanadium–porphyrin complexes contain the oxygen atoms of the vanadyl radical. Consequently, their polarity is increased and their R_f values decreased from those of the corresponding porphyrins.

Blumer (1956) also reported that even small structural differences were reflected in the movement of the porphyrin spots on a chromatogram. The decarboxylated form of desoxophylloerythrin, containing an isocyclic, five-membered ring, was readily separated from mesoetioporphyrin, which contains an open side chain and the same number of carbon atoms. The R_f values of typical porphyrins from bitumens, according to the data of Blumer (1956) are summarized in Table 3.

Paper-strip and sheet chromatographic methods were developed by Dunning and Carlton (1956) for separation of the porphyrin aggregates of crude oils into several distinct groups. These methods are of use in exploratory work and for studies of porphyrin properties, but do not supply enough of the porphyrin for further study. Larger quantities of the aggregate were, therefore, chromatographed on paper pulp to obtain sufficient quantities of the several groups for spectrophotometric studies; the groups were investigated further by paper-sheet chromatographic methods to estimate their purity and to identify them with the groups isolated in the preliminary paper-strip and -sheet methods.

The first two groups eluted from the paper-pulp column were characterized by spectra of the etio type, in which peak III (532 mμ) is stronger than peak II (565 mμ). Peak I (620 mμ) and peak IV (500 mμ) were displaced toward longer and shorter wave lengths, respectively, in the two most mobile groups. The other groups had phyllo type spectra; peak II was stronger than peak III. The wave length of the main fluorescence band changed about 2 mμ toward shorter wave lengths proceeding from the most mobile to the least mobile of the groups, paralleling the changes in absorption spectra. Representative samples of the several porphyrin groups were compared by paper-sheet chromatography. Correlations of spectral and chromatographic data indicated that the etio-type spectra of the two most mobile groups actually represented the presence of porphyrins similar to etioporphyrin III, rather than pyrroporphyrin, a plant porphyrin having a spectrum of the etio type.

TABLE 3.

Relative Movement (R_f) *Values of Porphyrin Materials on Paper Chromatograms*

(Whatman No. 3 paper; CCl_4-C_8H_{18}: 70–30)

Porphyrin	R_f Value
Mesoetioporphyrin	0.63
Desoxophylloerythroetioporphyrin-Ni	0.54
Desoxophylloerythroetioporphyrin	0.47
Desoxophylloerythroetioporphyrin-V	0.20
Desoxophylloerythrin-Ni-methyl ester	0.23
Desoxophylloerythrin-methyl ester	0.15
Desoxophylloerythrin-V-methyl ester	0.08
Mesoporphyrin-Ni-dimethyl ester	0.12
Mesoporphyrin dimethyl ester	0.10
Protoporphyrin-Cu-dimethyl ester	0.13
Protoporphyrin-Ni-dimethyl ester	0.10
Protoporphyrin dimethyl ester	0.07

The separation of the porphyrins having an etio spectrum is partial substantiation of the work of Treibs (1935a) who reported porphyrins having this type of spectrum in extracts of several bituminous materials. However, as discussed above, porphyrins of the hemoglobin series are fairly common in the plant kingdom. Therefore, these observations cannot be considered as proof that animal remains are involved in the origin of petroleum.

In addition to a large amount of decarboxylated porphyrin material, the paper-sheet chromatographic investigations of Dunning and Carlton (1956) indicated the presence of a porphyrin species containing one carboxylic acid group. Therefore, a group designated 7a (from the acidic portion of the aggregate) was investigated by the method of Nicholas and Rimington (1949). The solvent was 2,4-lutidine saturated with water used in the presence of ammonia vapor. The results are shown in Fig. 7. The R_f value (rate of spot movement relative to rate of front movement) of group 7a showed that this component of the porphyrin aggregate consisted of porphyrins containing one carboxylic acid group.

Paper-pulp chromatography affords a simple method of accomplishing the usually difficult separation of carboxylated and decarboxylated porphyrins. Preliminary steps have been taken in developing this method into a routine laboratory procedure. The peculiar geochemical significance of carboxylated porphyrins in petroleum, discussed below, lends importance to such work.

Isolation—Free porphyrins have not been identified in petroleum to date. Rather, the porphyrins are present as stable metal complexes.

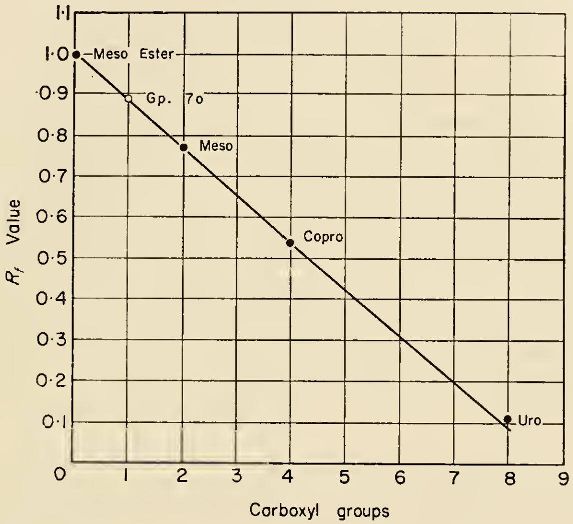


FIG. 7. Relation of R_f values to number of carboxyl groups in paper-sheet chromatography.

However, porphyrins have been identified in the pyridine extracts of coal by Treibs (1935a, 1935b) in amounts up to about 70 p.p.m. Blumer (1950), by means of HCl–*iso*propyl ether fractionation, identified free porphyrins in extracts of Swiss bitumens. Where free porphyrins occur in natural substances, they usually may be extracted with various polar solvents such as ether, acetic acid, or pyridine. Such methods are used extensively in clinical work for the extraction of porphyrins from faeces, bile, or urine. However, in most bituminous materials, the metal–porphyrin complexes are prevalent and even in the Swiss bitumens were present at a concentration 100 times that of the free porphyrins.

The isolation of porphyrin aggregates from crude oils depends upon removing the metals from the porphyrin complexes so that the central nitrogens may exhibit their basic characteristics. The porphyrins then may be separated from the crude oil components by physicochemical methods.

Procedures for removing their metal components from porphyrins have advanced little since the work of Treibs (1934b). Recently, however, Groennings (1953) published a revised and simplified procedure involving prolonged digestion of the crude oil with glacial acetic acid saturated with HBr in a sealed ampoule at 50°. The free porphyrins are basic and, therefore, are extracted from the digestion products by strong hydrochloric acid. Because of their typical isoelectric points, they may be separated from neutral or basic substances having different isoelectric points by buffering the solutions to a pH of 5, extracting into ether, and re-extraction into hydrochloric acid. This process may be repeated as often as seems desirable. Although this is basically an old procedure, it effectively takes advantage of the peculiar properties of porphyrins.

After the aggregate has been isolated, the porphyrin content may be determined colorimetrically or, more precisely, by a procedure in which the heights of the four peaks above background in the visible region are compared to those of a pure porphyrin sample. In this method, as used by Dunning and associates (1954), the concentrations of chloroform solutions of the porphyrin aggregates were determined by measuring the absorbance difference between the maximum and the two minima for each peak, averaging the results for the four peaks, and comparing with similar measurements of a pure porphyrin sample. The use of peak height above background rather than total peak height reduces errors from light absorption by nonporphyrin material. The porphyrin aggregate may consist of several different porphyrins, each with its own specific extinction coefficients for the four peaks. The four values of peak height above background were averaged to reduce errors caused by deviations of a single peak.

Although the vanadium– and nickel–porphyrin complexes are exceedingly stable, they may be partly decomposed by digestion under atmospheric pressure with the HBr–acetic acid solution for a few hours. Therefore, a "batch" extraction method was used by Dunning and Carlton (1956) to isolate large amounts of the porphyrin aggregate from a California crude oil rich in the nickel complex. This procedure is more suited to preparative than to analytical work. In this method, the crude oil is mixed with an equal amount of the HBr–acetic solution, heated to 50° and stirred while HBr is bubbled through the mixture. Then the separation is accomplished as before.

Metal–Porphyrin Complexes

One of the most important properties of the porphyrins is their ability to form complexes with many metals. The porphyrins are natural chelating agents of an efficiency seldom encountered in commercial or synthetic products with the exception of the phthalocyanines which have many properties in common with the porphyrins as shown by Linstead and Robertson (1936). The importance and occurrence of respiratory and photosynthetic pigments containing iron and magnesium porphyrin complexes have been discussed above. The formation of more stable metal complexes accounts for much of the geochemical importance of the porphyrins. The unusual stability of the vanadium and nickel complexes apparently is vital to the survival of porphyrin pigments in liquid bitumens.

Laboratory preparation—Methods for preparing many metal-porphyrin complexes were established several years ago. Hill (1925) used several means of preparing the metal–porphyrin complexes. The first, and most commonly used, of these consists of heating a porphyrin dissolved in acetic acid with a metal acetate. Other methods used by Hill (1925) and reviewed by Lemberg and Legge (1949, p. 93) were: heating the porphyrin with a metal salt in liquid ammonia, introducing sodium and potassium by means of the alcoholates in pyridine, the introduction of magnesium by the Grignard reagent, the use of metal oxides or carbonates in alcohol, and the use of metal salts in pyridine.

The first method of Hill (1925), which involves heating the metal acetate with the porphyrin in acetic acid, is simple and effective for the preparation of the stable metal–porphyrin complexes. The nickel–porphyrin complex commonly is prepared in this fashion and was prepared from a porphyrin aggregate by Dunning and associates (1953). Its ready preparation has allowed comparison with the natural nickel complex in crude oils. Treibs (1935a) prepared the vanadium-porphyrin complex by a difficult and inefficient procedure using VCl_4, a silver dish, and autoclaving.

The difficulties of synthesizing the vanadium–porphyrin complex in the laboratory had lent credence to the suggestion of Glebovskaya and Volkenshtein (1948) that the vanadium–porphyrin complex common to crude oils and other bituminous substances was the respiratory pigment of certain types of marine life, particularly the ascidians. This postulate seems unlikely inasmuch as it would involve such specific organisms in the origin of many widespread petroleum deposits. Recent work by Erdman and associates (1956) tends to discredit this unusual theory; they showed that the vanadium complex could be as readily synthesized as the nickel complex if the proper vanadium salt were used. Furthermore, Lemberg (1938) reported that no vanadium–porphyrin complex is known to occur in living animals. After an extensive study of the blood of ascidians, Webb (1939) reported that the vanadium chromogen of these organisms was in no sense a respiratory pigment and that it was not a porphyrin compound. Therefore, it appears likely that the vanadium–and nickel–porphyrin complexes were formed within the reservoir or source bed by metal exchange reactions with the common magnesium (chlorophyll) or iron (hemoglobin) respiratory pigments of plants and animals. This view is widely held by petroleum scientists, such as Blumer (1950), Dyemenkova and Kurbatskaya (1955), Scott and associates (1954), and Treibs (1935a). Milroy (1909) studied the preparation of nickel– and tin-porphyrin complexes directly from hemin. This procedure is effective if reducing conditions apply, and efficacy of the method points to the credibility of the metal-displacement postulate because reducing conditions normally prevail in petroleum reservoirs. Another possibility that has been largely overlooked is the fomation of the nickel– and vanadium–porphyrin complexes from the free porphyrins that are rather widespread in nature as discussed above. Recently Bases (1957) reported the synthesis of the uranyl–protoporphyrin complex by the methods discussed above, although this complex probably involves the carboxyl rather than the nitrogen groups.

The stabilities of the metal–porphyrin complexes vary greatly and depend primarily upon the metallic constituents. According to older reports summarized by Lemberg and Legge (1949), sodium, potassium, and arsenic are displaced from their porphyrin complexes by water; magnesium, and lead by dilute acetic acid; silver, zinc, and divalent iron and tin by hydrochloric acid; copper, trivalent iron, nickel, and cobalt by the action of concentrated sulfuric acid; tetravalent tin and aluminum cannot be removed. More recent studies of Caughey and Corwin (1955) show that iron, cobalt, nickel, and zinc are displaced from their complexes with mesoetioporphyrin by concentrated sulfuric acid without decomposition of the porphyrin.

Erdman and associates (1957) have made observations of vital geochemical interest concerning the stabilities and the kinetics of displacement of copper, zinc, iron, nickel, and vanadium from their porphyrin complexes. These investigators developed a procedure for separating the complexes from mixtures, based on their rate of reaction in a homogeneous system of benzene, acetic acid, and a halogen acid. In this system, zinc and divalent iron are removed from their complexes by 0.4 M HCl, nickel by 0.08 M HBr, trivalent iron by 0.8 M HBr, and vanadyl (VO) by 2.6 M HBr. Although bituminous systems are notorious for their anomalous behavior and this method was developed using pure porphyrin samples, the technique may prove satisfactory for the study of bituminous extracts. If so, the method will be of the order of importance of the method originally developed by Treibs (1934a, 1934b) for the gross separation of the metals from the porphyrin aggregate. Whether or not this proves to be the case, the method and related kinetic data shed new light on the stabilities of the porphyrin complexes.

Identification—The metal–porphyrin complexes usually are identified in bituminous extracts by their distinctive spectra in the visible region (Fig. 8). The porphyrin complexes commonly have a major and minor peak in the visible region between 510 and 580 mμ, and a very strong peak at about 400 mμ which often is obscured by colorless substances that have strong absorbance at lower wave lengths. Beach and Shewmaker (1957) report that measurements of the heights of the visible peaks above background give simple and reasonable estimates of complex contents for extracts of moderate optical purity. However, the total absorbance at the point of maximum absorbance is a very unreliable indication of concentration unless the complex is optically pure.

Spectra. Hill (1925) distinguished among three types of spectra of metal–porphyrin complexes. Those of the alkali metals and thallium resemble the acid porphyrin spectrum because the longer wave length band is weaker than the second band. The second type has two absorbance peaks of about equal intensity, and the third type, typical of the more stable forms, has the stronger peak at the longer wave length. Several theoretical discussions have been presented on the correlations of the various types of spectra. For details, reference may be made to the works of Hill (1925) and Glebovskaya and Volkenshtein (1948), and to the more recent treatments of Aronoff (1950), Williams (1956), Caughey and Corwin (1955), and Erdman and associates (1957).

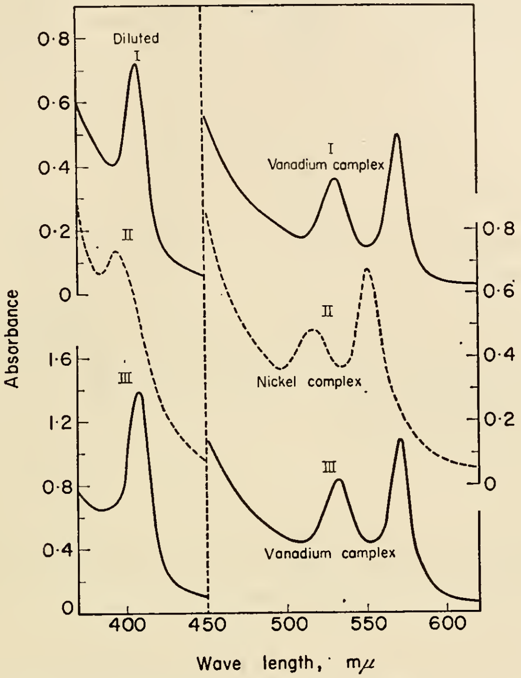


FIG. 8. Absorption spectra of final chromatographic fractions of crude oil raffinate. 3.0 mg per ml of benzene.

The spectra of metal complexes of some common porphyrins are summarized in Table 4.

The spectra of complexes of mesoporphyrin IX dimethyl ester with various metals, according to the measurements of Stern and Dezelic (1937), are summarized in Table 5.

Recent work of Erdman and associates (1956) has shown the major peak of the vanadium complex to be very sharp, as is probably also true of other important complexes. Therefore, the use of extinction coefficient values

TABLE 4.

Absorption Spectra of Common Metal Complexes of Etioporphyrins

Metal	Porphyrin Type	Solvent	Absorption Maxima, $m\mu$ I	II	Reference
VO*	Etioporphyrin I†	Dioxane	570	534	E*‡
VO	Etioporphyrin I	Pyridine	572	537	E
VO	Mesoetioporphyrin	Dioxane	570	533	E
VO	Mesoetioporphyrin	Pyridine	573	537	E
Ni	Etioporphyrin I	Dioxane	551	516	E
Ni	Mesoetioporphyrin	Pyridine	550	514	C**
FeOH	Etioporphyrin I	Dioxane	587	563	E
Cu	Etioporphyrin I	Dioxane	564	523	E
Cu	Mesoetioporphyrin	Pyridine	560	523	C

* The vanadium complex prepared synthetically contains vanadium as the vanadyl radical as shown by infrared studies of Erdman and associates (1956).

† An isomer of mesoetioporphyrin (Etioporphyrin III).

‡ Erdman and associates (1957).

** Caughey and Corwin (1955).

TABLE 5.

Absorption Spectra of Metal Complexes with Mesoporphyrin IX Dimethyl Ester

Metal	Solvent	Absorption Maxima: Wavelength, $m\mu$ I	II	Extinction Coeff. $\times 10^{-4}$ I	II
Pd	Dioxane	544	510	4.79	1.38
Ni	Dioxane	550	514	3.48	1.18
Ag	Dioxane	556	523	1.96	1.41
Cu	Dioxane	561	525	2.57	1.37
Hg	Dioxane	564	534	1.02	1.09
VO	Dioxane	570	533	2.61	1.46
Zn	Dioxane	570	534	2.01	1.81
Pb	Dioxane	580	531	1.30	0.35
CoCl	Benzene	549	—	2.15	—
GaCl	Benzene	572	534	2.25	1.57
InCl	Benzene	578	540	1.97	1.99
$SnCl_2$	Benzene	578	540	1.82	2.14
$GeCl_2$	Benzene	578	540	1.59	1.73
TiCl	Benzene	580	544	1.22	1.80

* Data of Stern and Dezelic (1937) and according to review of Lemberg and Legge (1949).

determined in other laboratories may involve considerable errors unless the instruments used are very similar. The molar extinction coefficients listed should be used with this reservation.

Isolation, occurrence, and geochemical significance—Several methods for isolation of metal–porphyrin complexes from crude oils, oil shales, and coal have proved quite effective. In general, effectiveness decreases rapidly with decreasing porphyrin content. With oils containing so much porphyrin–metal complex that it could be observed directly, Treibs was able to obtain complexes which he considered to be quite pure. The optimum combinations of methods, with oils of the United States, seldom produce extracts containing over a few percent of the complex. However, the impurities remaining often are of low light-absorbing properties so that very good spectra are obtained. This peculiarity probably results from the fact that the methods of observing separation commonly are based on light absorbance. Some of the most promising methods for the isolation of porphyrin–metal complexes from bituminous materials are discussed below.

Alfred Treibs (1934a, 1934b, 1935a, 1935b), in his pioneering research on the occurrence of porphyrins in bituminous materials, developed many of the methods that are still used today. It is an interesting historical note that Dhere and Hradil (1934) independently discovered the presence of porphyrin materials in a Swiss bitumen. A note by Dhere (1934) and comments by Treibs (1935a) show that these scientists had observed porphyrins in bitumens before the publication of Treibs' first *porphyrin* paper (1934a). Treibs, in an earlier paper, (1933) had tentatively identified similar substances as anthraquinone dyes. It appears, however, that Treibs actually had correctly identified the porphyrins in bituminous extracts a few months prior to their independent discovery by Dhere and Hradil, who used fluorescence spectra as well as light absorption measurements for their identification. This work of Dhere and Hradil (1934) has gone almost unnoticed, probably because Treibs continued such studies after his original discovery while Dhere concentrated on the fluorescence of biological materials.

Although Treibs is most famous for his digestive method of isolating the porphyrin aggregates (discussed above) he also used solvent extraction and chromatographic procedures extensively. In one procedure (1934a), he repeatedly extracted powdered shale with acetic acid at 100° evaporated the extract to dryness, washed it with water to remove the salts, and dissolved the residue in chloroform. In this study the final extract was digested with HBr–glacial acetic acid to obtain the porphyrin aggregate without an attempt to identify the complexes in the original extracts. Desoxophyllerythrin and its etioporphyrin were the main porphyrins identified. Later work on these porphyrins led Treibs (1934b) to the conclusion that a mesoporphyrin type also was present. The identification of the plant porphyrins is generally accepted, but his identification of mesoporphyrin has been seriously questioned. From his comments it is apparent that Treibs (1934b) was aware of the similarity of the spectra of pyrroporphyrin and porphyrins of the hemoglobin series. He believed that his other chemical and physical tests showed that this porphyrin was not pyrroporphyrin. Whether or not this is the case remains to be proved. Furthermore, the occurrence of porphyrins of the hemoglobin series in the plant kingdom complicates any concrete conclusions that may be drawn from porphyrin research regarding the presence of animal remains in bituminous materials. Treibs (1934b) also identified metal–porphyrin complexes and, in some cases, free porphyrins in ether–pyridine extracts of bituminous rocks, asphalts, and mineral waxes. His identification of the vanadium–porphyrin complex has been corroborated by later studies of Glebovskaya and Volkenshtein (1948), Skinner (1952) and Dunning and associates (1953, 1954). However, his identification of the iron–porphyrin complex in an oil shale has been contradicted by Glebovskaya and Volkenshtein (1948) who established the presence of the nickel–porphyrin complex in an oil shale and believed that this was the complex reported by Treibs (1934b) as the iron–porphyrin complex. The presence of the nickel–porphyrin complex in petroleum was established by Dunning and associates (1953). Further work by Moore and Dunning (1955) on extracts of a Colorado oil shale corroborated Glebovskaya and Volkenshtein's (1948) identification of the nickel–porphyrin complex in oil shale. However, this work also indicated that Treibs' (1934b) identification of the iron–porphyrin complex probably was correct. The data on which this conclusion was based are summarized in Table 6, taken from the paper by Moore and Dunning (1955).

TABLE 6.
Metal and Porphyrin Contents of Oil-shale Extracts
(weight percent, average of two extractions)

Material	Extract		
	Benzene	Benzene–methanol	Pyridine
Iron	0.030	0.073	0.126
Nickel	0.0059	0.0082	0.0137
Vanadium	0.0006	0.0082	0.0035
Copper	0.0006	0.0022	0.0086
Porphyrin aggregate	0.133	0.249	0.040
Nitrogen	0.96	1.45	2.63*

* Freed of pyridine by azeotropic distillation.

The ratio of porphyrin to metal in complexes with iron, nickel, or vanadium is about 10:1 on a weight basis. Therefore, insufficient nickel or vanadium was identified to complex with all the porphyrin aggregate in any of the extracts with the exception of nickel in the pyridine extract. More than fifty metals other than iron, nickel, vanadium, and copper were determined semiquantitatively in these extracts. Of these metals, only sodium and calcium were present in sufficient quantities to complex an appreciable part of the porphyrin aggregates, however, sodium and calcium form unstable complexes with porphyrins. In petroleum much of the iron detected may be of an adventitious nature, but the immobility of organic matter of oil shale reduces this probability with oil–shale extracts. The above data provide evidence that much of the porphyrin aggregate of this oil shale probably is present as an iron–porphyrin complex.

Recently, Sugihara and McGee (1957) identified a nickel–porphyrin complex in gilsonite. This bituminous substance is reported to contain about 300 p.p.m. of this complex, apparently containing desoxophylloerythrin as the porphyrin component.

Treibs (1934b) observed that when pheophytin was heated to 250–320° in petroleum, phylloerythrin was formed. Further heating to 360° resulted in the decarboxylated form of desoxophylloerythrin. These and later studies provide strong evidence of the importance of plant remains in the formation of bituminous substances.

Treibs (1935b) detected porphyrins and their metal complexes in quantities ranging up to about 70 p.p.m., in the pyridine extracts of most samples of coal studied. It was observed that the decarboxylated forms were most common, acidic porphyrins being detected in only a few samples. The porphyrin type most common to these extracts was identified by him as deuteroetioporphyrin. Because this identification was based mainly on spectral studies, it can be considered only tentative. Desoxophylloerythrin, common in oil shales and petroleum, was found only in cannel and boghead coals. This study of Treibs (1934b) included many German and European coals and also coals from Scotland, Australia, America and Africa. The vanadium–porphyrin complex was found only in a boghead coal and in torbanite, but the complex which he identified as the iron–porphyrin complex was quite common.

In a general review of his work Treibs (1936) reported that metal–porphyrin complexes were found in 66 crude oils, 9 asphalts, 4 earth waxes, and 5 asphaltites. Seventy bituminous oil shales, 8 phosphorites, 1 guano, 7 cannel coals, and 17 coals contained both metal–porphyrin complexes and green pigments, and 14 sapropels contained only the green pigments. A Swiss oil shale was richest in metal–porphyrin complexes, containing up to 4000 ppm. The richness in porphyrins of Swiss oil shale is attested to by the work of Blumer (1950), who reported 3800 ppm of porphyrin complexes in this substance.

Free porphyrins were identified by Treibs (1935b) in some coal samples as well as in bituminous rocks but most of the porphyrins generally were present as metal complexes. Furthermore, the chlorophyll derivatives were more common and the porphyrin constituents usually were of the decarboxylated types except in "Eastern burning shales". These shales were of Cambrian and Devonian ages and petrographic studies indicated that only moderate temperatures and pressures had prevailed during their development. Treibs (1935a) reported that phosphorites contain the same porphyrins as petroleum and oil shales, but the amount of acidic porphyrins often exceeded those of the decarboxylated porphyrins.

More recently, Glebovskaya and Volkenshtein (1948) studied the spectra of alcohol and chloroform solutions of petroleum and bituminous extracts. These workers concluded, mainly on the basis of earlier literature, that porphyrins occur free or as metal complexes in bitumens, and that the free porphyrins belong to the chlorophyll series. The fact that free porphyrins have not been identified in petroleum samples is worthy of repetition; they are limited to rather rare samples of bituminous shales. These workers observed the presence of the vanadium-porphyrin complex and, as discussed above, identified the nickel–porphyrin complex in some of their extracts.

Because much of the work on porphyrins has been done by organic chemists, crystallization has been a favorite tool. The work of Glebovskaya and Volkenshtein (1948) indicates that the success of such procedures should be judged with a great deal of caution. They noted that distillation (partial) of alcohol extracts of crude oil was accompanied by the separation of "dark red platelets". These might be viewed as crystals and expected to be pure, however, examination of the spectra published by Glebovskaya and Volkenshtein (1948) shows that these platelets contained large amounts of impurities.

The invalidity of the conclusions of Glebovskaya and Volkenshtein (1948) that the vanadium–porphyrin complex was the respiratory pigment of certain marine species has already been noted. Blumer (1950) studied solvent extracts of Swiss bitumens from the Serpiano deposit, identifying the vanadium–porphyrin complex and observing that only about one-tenth of the total vanadium was complexed with porphyrins. This is the converse of vanadium-poor Colorado oil shale extracts but is parallel to the relative vanadium and porphyrin contents of many crude oils as discussed below together with more extensive data.

The presence of free porphyrins in the extracts of the Swiss bitumens was also observed by Blumer (1950). These were present to the extent of about 1 percent of the complexes and were determined by careful fractionation of an isopropyl ether solution with hydrochloric acid. This work is recent and done quite precisely, therefore, it corroborates the earlier reports of Treibs to the effect that free porphyrins sometimes occur in rare bituminous samples.

Propane-precipitation results in the separation of a considerable amount of porphyrin–metal complexes from the major portion of a crude oil (raffinate) because these complexes are mainly associated with the asphaltic portion of petroleum. Extracts relatively rich in porphyrin complex are obtained when this precipitation is followed by extraction of the precipitated asphalt with solvents of increasing polarity. This method was used by Skinner (1952) in a study of crude oil from the Santa Maria Valley (Calif.). Examination of his results shows that the vanadium–porphyrin complex is scattered throughout several extracts of the asphalt of this crude oil and even, in small amounts, in the propane-soluble portion. His results of the distribution of vanadium in the several fractions are of considerable interest and are summarized in Table 7.

TABLE 7.

Vanadium Contents of Successive Extracts of Santa Maria Valley Crude Oil

Data of Skinner, 1952

Fraction	Weight, grams	Vanadium		
		In extract wt. percent	In extract grams	Total in crude wt. percent
Whole crude oil	202.5	0.0181	0.0366	100.0
Propane soluble	116.0	0.00024	0.00028	0.76
Propane insoluble	86.5	0.042	0.0363	99.18
Total	202.5		0.03658	99.94
Pentane soluble	51.4	0.010	0.00514	14.05
Hexane soluble	3.2	0.037	0.00119	3.25
Heptane soluble	1.0	0.052	0.00052	1.42
isoOctane soluble	0.2	0.057	0.00011	0.30
Cyclohexane soluble	13.7	0.066	0.00904	26.08
Benzene soluble	14.9	0.096	0.01430	39.08
Pyridine soluble	0.6	0.16	0.00096	2.62
Total	85.0		0.03126	86.80

These results show that much of the vanadium can be removed from a crude oil by propane precipitation; less than 1% of the vanadium originally present remained in the propane-soluble portion. It is significant, however, that the presence of vanadium and the vanadium–porphyrin complex can be detected in the raffinate. Garner and associates (1953) and Dunning and Rabon (1956) reported similar results with other oils.

Dunning and Moore (1957) made a systematic study of the precipitation of asphaltic materials from a Midcontinent crude oil by propane. This work agreed with that of other workers in showing that much of the vanadium was removed from the crude oil by propane precipitation but that some remained in the raffinate. Most of the recent investigators have confined their experimental efforts to metal determinations and have limited their porphyrin identifications to approximations based on spectra showing the presence of porphyrin complexes. The work of Blumer (1950), cited above, is an exception of this generalization in that he was interested primarily in geochemical considerations rather than in process development. In their studies, Dunning and associates (1953, 1954, 1955, 1956) devoted most of their attention to actual porphyrin analyses by the method of Treibs (1935a) and Groennings (1953). The distribution of nickel, vanadium, and porphyrins in fractions obtained by propane precipitation of a Midcontinent crude oil are summarized in Table 8.

TABLE 8.
Metal and Porphyrin Contents of Crude Oil Fractions

	Crude oil wt.%	Raffinate wt.%	Asphaltenes wt.%
Nickel	0.0055	0.0003	0.0245
Vanadium	0.0110	0.0004	0.0450
Porphyrin aggregate	0.0200	0.0025	0.1000

The distribution of porphyrin aggregate and metal–porphyrin complexes among alcohol-soluble portions of extracts of a crude oil from the North Belridge field (Calif.) were reported by Dunning and associates (1953). These extracts were obtained by extraction of a propane-precipitated asphalt with solvents of increasing polarity. Porphyrin aggregate contents were determined by actual isolation, and the nickel–porphyrin complex concentrations by a spectral method similar to that of Beach and Shewmaker (1957). The results are summarized in Table 9.

TABLE 9.
Relative Concentrations of Metal–Porphyrin Complexes and Porphyrin Aggregates in Alcohol-Soluble Portions of Successive Extracts

Extract	Metal–porphyrin complex		Porphyrin aggregate
	Experimental	Skinner†	
Propane	0.31	0.12	0.07
Pentane	0.56	0.24	0.59
Hexane	1.00	1.00	1.00*
Heptane	1.24	1.44	3.75
isoOctane	0.72	0.23	—
Cyclohexane	0.63	0.63	1.07
Benzene	0.63	0.57	1.14
Pyridine	0.27	0.38	—

* Concentration = 700 p.p.m.

† Data calculated approximately from spectra of Skinner (1952), Santa Maria Valley oil.

These data show that, like the vanadium–porphyrin complex, the nickel–porphyrin complex is distributed throughout the various crude oil extracts.

Because the nickel–porphyrin complex had not previously been identified definitely in crude oils, the spectral data indicating its presence were corroborated by further experiments. As a final step in the proof of structure, the nickel complex was synthesized from the porphyrin aggregate of this crude oil. This apparently was the first synthesis of a porphyrin complex from the porphyrin aggregate of a bituminous substance, therefore, details of the method will be described. Nickel carbonate was heated in glacial acetic acid until gas was no longer evolved. The dried porphyrin aggregate was then added to this solution and the mixture refluxed gently for 15 min. The acetic acid was distilled off under vacuum and the residue dissolved in ether. The solution then was washed with water several times and with 7% hydrochloric acid to remove the unreacted porphyrin. Finally, the absorption spectrum was determined.

Figure 9 shows the spectra of the alcohol-soluble portions of several extracts of the North Belridge asphalt. The presence of a metal–porphyrin complex is shown in each of the extracts. The similarity of the peak locations to those of the nickel–porphyrin complex is evident. The spectra of the extracts and the synthetic nickel–porphyrin complex had a major peak at about 550 mμ and a minor one at about 510 mμ. The synthesis of the nickel–porphyrin complex and comparison of its properties with those of the porphyrin-rich extract completed the identification of the nickel-porphyrin complex in this crude oil according to classical methods of qualitative organic analysis.

Work of Erdman and associates (1956) and Dunning (1953) showed that the porphyrins and their complexes generally are interfacially active. As a result, they might be expected to be concentrated at interfaces, and Dunning and associates (1954) used the water-spray method of Bartell and Niederhauser (1949) in an attempt to concentrate the porphyrin–metal complexes of the North Belridge oil. This procedure, combined with pentane-extraction methods, resulted in the isolation of several fractions the properties of which are shown in Table 10.

Correlations of these data are made more readily apparent by referring to Fig. 10, in which the nickel and vanadium are added to obtain the "metal" values, and *RAF*, *PS*, and *PI*, are the extracted crude oil, pentane-soluble, and pentane-insoluble portions of the water-spray extract, respectively.

The large excesses of metals and nitrogen over that accounted for by the metal–porphyrin complex contents of these extracts points to the postulate that other metal–nitrogenous substances may be present. Lemberg and Legge (1949) report that several decomposition products of the porphyrins form relatively stable complexes with metals. Some of these are discussed below in the section on bile pigments. Such decomposition products would not be identified as porphyrins because of their different light absorption characteristics. However, several of these have other physical

TABLE 10.

Properties of Water-Spray Fractions of a California Crude Oil

Fraction	Percentage of oil	Ash	Composition, wt. % Ni	V	N	Porphyrin aggregate
Whole crude oil	100.0	0.039	0.0083	0.0023	0.76	0.0485
Extracted crude oil	76.7	0.037	0.0079	0.0023	0.68	0.0420
Pentane solubles of extract	15.5	0.034	0.0044	0.0013	0.66	0.0390
Pentane insolubles of extract	1.8	1.38	0.0400	0.0114	2.38	0.1550
Water-soluble extract	0.6	—*	0.0100	0.0022	—*	—*

* Not detectable.

properties similar to the porphyrins and would be expected to react in the extraction process in a manner similar to the porphyrins.

The nickel and vanadium contents were increased more than the porphyrin or nitrogen contents in the pentane-insoluble portion of the water-spray extract. Apparently part of these metals in the crude oil was not complexed with large nitrogenous molecules. This is in agreement with Garner and associates (1953). The rather high (0.01 wt. %) nickel concentration in the water-soluble extract provides further evidence that the crude oil contained uncomplexed nickel.

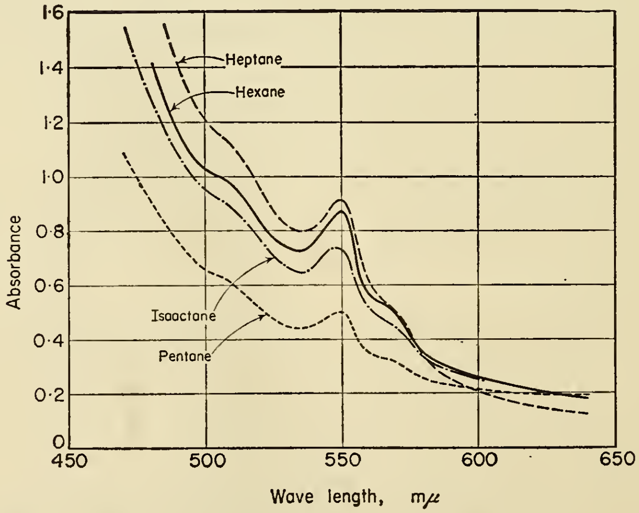


FIG. 9. Absorption spectra of alcohol-soluble portions of successive extracts of crude oil.

The nitrogen, nickel and vanadium contents of these water-spray extracts vary in the same manner as do the porphyrin contents. The ratios of porphyrin contents to the total nickel and vanadium contents are 3.0, 4.6, 4.1 and 6.8 in the propane-insoluble extract, whole crude oil, extracted crude oil, and propane-soluble extract, respectively. As mentioned above, the ratio of porphyrin to vanadium or nickel in a porphyrin complex is about 10 to 1. Thus, insufficient porphyrin was isolated in any of these fractions to complex all of the nickel and vanadium present.

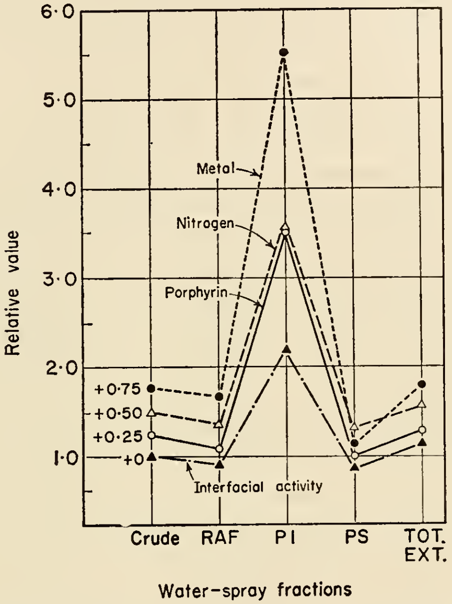


FIG. 10. Relative values of properties of water-spray fractions.

Extensive chromatographic and solvent-extraction procedures may produce petroleum extracts which contain vanadium primarily in the form of the vanadium–porphyrin complex. This observation has led to some misinterpretations in the literature. It should be emphasized that such extracts, containing vanadium primarily as the porphyrin complex, are rather commonly obtained from crude oils that do not contain enough porphyrin to complex even a major part of the vanadium present. The possibility remains that the remainder of the vanadium *may* be associated with materials of the porphyrin type that do not exhibit the usual porphyrin properties because of their complexity. This, however, is only a postulate and is supported only by circumstantial evidence. For the present, it must be concluded that much of the vanadium of most crude oils is *not* complexed with substances capable of extraction as porphyrins by current methods.

One of the most interesting questions on the origin and evolution of petroleum is that of the geochemical relationships between asphaltic and paraffinic oils. One group of geochemists attributes the asphaltic constituents to primary formation and regards such substances as the remnants of organic materials which, during the evolution of the oil, simplify to form the lighter, more paraffinic oils. Another group maintains that the tarry substances are of a secondary character and probably arise as a result of microfloral activity. The latter view has found little support but recently has been discussed by Radchenko and Sheshina (1955) who reported that the vanadium complexes were associated with the asphaltic substances of crude oils, and that the nickel–porphyrin complexes were associated with the oleaginous components. According to these authors, more than 90% of the porphyrins in petroleums with a high sulfur content were present as vanadium complexes, while in low-sulfur oils they were present as nickel complexes. Furthermore, they reported that the vanadium–nickel ratio was higher in oils of high sulfur contents. From these results they concluded that the concentration of sulfur, porphyrins, and vanadium in petroleum was a secondary process caused by bacterial action. However, they believe that the nickel–porphyrin complexes were related to the biochromes of the organisms originally present during the formation of the oil. These conclusions seem illogical from a philosophical approach and doubtful even if the data are accepted as being generally applicable. A more recent publication of Radchenko and Sheshina (1956) is especially interesting with regard to the generality of their earlier conclusions. In a study of porphyrins in the organic matter of sedimentary rocks, these authors corroborated their earlier report that the vanadium-porphyrin complexes were mainly associated with the asphaltic fractions. However, the nickel–porphyrin complexes of the sedimentary rock extracts were distributed throughout the several fractions in contradistinction to results of their petroleum studies which showed that the nickel-porphyrin complexes were exclusively in the oily (as opposed to asphaltic) fractions. Despite this apparent disagreement with part of their earlier work, Radchenko and Sheshina maintain that there is a real distinction between the genesis of the vanadium– and nickel–porphyrin complexes in bituminous materials and that the vanadium–porphyrin complexes are of secondary nature. However, they are practically alone in this contention differing with most American geochemists and with other Russian scientists such as Glebovskaya and Volkenshtein (1948) who studied similar materials, and Dyemenkova and Kurbatskaya (1955) who reviewed the results of several workers.

The North Belridge oil discussed above is unusually rich in nickel–porphyrin complexes, contains 3.6 times as much nickel as vanadium, and contains a moderately large amount of sulfur, 1.14%. The sample is not typical of the field, being produced from a shallow formation of Pleistocene age. The Midcontinent oil referred to above is produced from a sand of Pennsylvanian age in southern Oklahoma. This oil contains about twice as much vanadium as nickel (Table 8) and most of the porphyrin content is present as a vanadium complex. Furthermore, the sulfur content is 1.54%, nearly equal to that of the North Belridge sample. These data were determined by Dunning and associates (1953, 1954, 1956, 1957) and include actual isolation of the porphyrin aggregate as well as estimates of metal–porphyrin complex contents from spectral measurements. The Santa Maria Valley crude oil contains mainly the vanadium-porphyrin complex, about twice as much vanadium as nickel, and high sulfur content (5.0%). These examples illustrate the danger of drawing generalizations from data involving incomplete studies or too few oils.

Some data of Garner and associates (1953) are instructive as to the relationship of vanadium–nickel ratio and sulfur content. These are summarized in Table 11.

TABLE 11.

Vanadium, Nickel, Sulfur, and Asphaltene Contents of Venezuelan and Middle East Crude Oils

per cent, data of Garner and associates (1953)

Crude oil	Vanadium	Nickel	V/Ni	Asphaltene*	Sulfur
Venezuelan	0.02720	0.000394	69.0†	8.24	1.51
Iran	0.00299	0.000658	4.5	0.82	1.02
Agha Jari (Iran)	0.00302	0.000821	3.7	1.80	1.08
Iraq A	0.00205	0.000819	2.5	1.30	1.32
Iraq B	0.00242	0.00114	2.1	2.50	1.64
Kuwait	0.00205	0.000557	3.7	0.91	2.04
Damman (Saudi Arabia)	0.000404	0.000114	3.6	1.00	0.62
Abqaiq (Saudia Arabia)	0.000296	0.0000512	5.8	0.50	0.56
Abqaiq-Damman	0.000343	0.0000659	5.2	0.38	0.90
Qatar	0.000528	0.000141	3.7	1.10	1.25

* Portion insoluble in hexane, soluble in benzene.

† Nickel value probably is low.

Although these data refer to vanadium and nickel contents, and are unrelated to porphyrin contents, it is apparent that the vanadium–nickel ratio is not a direct function of sulfur content. Furthermore, they corroborate the porphyrin studies cited above. As a result of their studies, Garner and associates (1953) concluded that, although there was no precise relationship between vanadium and asphaltene contents, high asphaltene content was associated with high vanadium content.

In a study of a series of Cretaceous oils from Canada, Scott and associates (1954) reported data showing a direct relationship of the vanadium contents with specific gravities and with the carbon residues of several samples. Such observations appear to be the general rule.

Treibs (1935a) first used chromatographic methods for the isolation of porphyrin complexes from extracts of oil and other bituminous substances.

Although his separations were conducted carefully and with great patience, the results probably are not as good as may be obtained with the excellent adsorbents and techniques available today. Chromatographic methods should suffice for the isolation of porphyrins from crude oils, however, crude oil is a quasi-colloidal system and does not necessarily obey the physical principles upon which chromatographic theories and methods are based. Chromatographic separation is made more efficient and rapid by denaturation of the crude oil by processes such as solvent precipitation preceding chromatographic separation.

One chromatographic zone containing a nickel–porphyrin complex and two zones containing vanadium–porphyrin complexes were isolated by Dunning and Rabon (1956) from the raffinate resulting from the propane precipitation of an asphaltic Midcontinent crude oil. The isolation procedure involved extensive chromatography using silica gel and alumina columns. The spectra of the complexes isolated are shown in Figure. 8. Alumina was more effective for separating the metal–porphyrin complexes from the non-porphyrin material than was silica gel, however, use of silica gel permitted a better separation of the nickel–porphyrin complex from the vanadium–porphyrin complex. Alternate silica gel and alumina chromatograms were effective for the separation of the metal complexes from each other and from light-absorbing impurities. The spectral identifications were corroborated by decomposing the complexes and determining their metal and porphyrin contents.

The metal contents of metal–porphyrin extracts presumably could be determined by usual methods of analyses, however, the amounts of relatively pure extracts are normally very small so that micro methods are required. Among the methods used by Dunning and associates (1953, 1954, 1956, 1957) are emission spectroscopy, spectrography, flame photometry, X-ray spectrography, and colorimetry as developed by Wrightson (1949). Each of these methods, with the exception of the X-ray spectrograph, destroys the valuable samples. The flame photometric method of Whisman and Eccleston (1955) was found most useful for the determination of nickel in extracts practically free of other metals. Quantitative determinations were made by comparison of emission intensities of the sample with those of pure samples under identical conditions. The amounts of metal thus determined agreed closely with the amounts calculated from the absorbance of the nickel-complex samples and the extinction coefficient of the pure complex.

The X-ray spectrograph, equipped with a helium path, appears to afford a promising method for both vanadium and nickel analyses. Only small samples are required and the method is being developed to supply rather precise data. In one study, Dunning and Rabon (1956) reduced porphyrin-rich extracts to viscous tars and smeared them on Mylar films stretched over standard sample holders. Vanadium was identified by observation of the $K\alpha$ emission at 2.505 Å and $K\beta$ emission at 2.285 Å. Semiquantitative estimations were made by calibration with samples that had been analyzed spectrographically by several laboratories. Results were in agreement with the calculated values. The emission spectrograph was used for larger samples of lower purity. Inasmuch as vanadium complexes are quite volatile, the ashing procedure is critical and best results were obtained by wet ashing methods.

Studies by Dunning and associates (1953, 1954, 1956) show that both the nickel and vanadium complexes are principally associated with the asphaltic components of crude oils, however, both complexes also are found in smaller amounts in the oleaginous portion of a Midcontinent and California crude oils. This work indicates no sharp distinction between the properties of vanadium– and nickel–porphyrin complexes and indicates a close relationship of these materials with the original source of petroleum. With few exceptions, appreciable porphyrin contents in the oils studied are limited to highly asphaltic oils from reservoirs of geologically "new" ages. The porphyrin contents of "clean paraffinic" American oils such as Bradford, Oklahoma City, Wilcox, and Bartlesville crude oils are very low.

The results of Garner and associates (1953) and Woodle and Chandler (1952) corroborate the above observations, and both of these groups of authors conclude that the constancy of the vanadium–nickel ratios in their various extracts indicates that most of the vanadium and nickel of crude oils are in similar forms. The experimental results showing a relationship between vanadium and sulfur observed by Radchenko and Sheshina (1955) probably are correct for the formation studied, however, it is a common observation that correlations which are sound in one reservoir often do not hold in other petroleum producing formations. A general relationship between metal, ash content, nitrogen, sulfur, asphaltene, and porphyrin contents is to be expected because these substances have a common high degree of polarity compared to the strictly hydrocarbon constituents of petroleum or bituminous materials.

These laboratory results support the view that the asphaltic components of crude oils generally are of a primary character and that the porphyrin complexes are related to the original organisms and new formations originating during the sedimentation phase and the period of diagenesis before the petroleum moves from its source bed. This is in agreement with the conclusions of Scott and associates (1954) in a study of the trace metals of Canadian oils, Treibs (1934b, 1935a) in porphyrin studies of a large number of Caucasian oils and bitumens, Blumer (1950) in studies of sediments and bituminous substances and Dyemenkova and Kurbatskaya (1955) in a review of work with crude oils and solid bitumens of petroleum series, and several other workers such as Glebovskaya and Volkenshtein (1948), and Skinner (1952).

In certain exceptional instances, it appears that substances of asphaltic appearance may be formed from clear crude oils by secondary processes such as weathering and oxidation of oil seeps. The loss of volatile components and the processes of oxidation and perhaps polymerization sometimes result in the conversion of a light oil to a heavy viscous one. Such processes normally would result in decreased porphyrin content. Recent studies have indicated some possibility of differentiating between such substances and the asphaltic constituents of "young" crude oils by porphyrin analyses. If this can be done, the results would be of considerable value in petroleum exploration.

Possible sources of the rather common vanadium–porphyrin complex were discussed above. The postulate that it is the respiratory pigment of certain types of marine life has been discredited by many workers, but the well-known high concentrations of vanadium in the ascidians still may cause speculation that they are instrumental in accounting for the high content of vanadium in some bituminous substances. Blumer (1952), after an extensive study of the inorganic materials of bituminous rocks, concluded that although inorganic constituents are concentrated by living organisms, this probably was not the mechanism primarily responsible for the high metal concentrations of bituminous materials. Rather, the trace elements from sea water are collected by the decomposition products of organisms. Based on data presently available, this rather conservative view appears to be the most valid conclusion.

Treibs (1934b, 1935a) has emphasized that the presence of carboxylated porphyrins in petroleum is evidence of a low-temperature history of the reservoirs with which they are associated. This conclusion was based on observations that pure porphyrins were decarboxylated at temperatures from 300° to 350°. The reaction occurs at even lower temperatures over extended periods. Although the effect of high pressures in inhibiting decarboxylation should be considered, the presence of carboxylated porphyrins in crude oils is evidence that these crude oils and their source materials have not been subjected to high temperatures. Porphyrins have not been identified in all oils and, indeed, are quite rare in the older American crude oils. Therefore, it would be premature to assume low-temperature origins for all crude oils.

Although much of the porphyrin content of crude oils and bituminous substances is of a decarboxylated form, the presence of carboxylated forms in small amounts is rather widespread. The "acid number" (Willstatter and associates, 1913) of fractions of the porphyrin aggregate was used by Treibs (1935a) to show the presence of acid porphyrins in several samples. This method is not particularly precise and requires considerable experience for proper interpretation. However, paper chromatographic methods such as those used by Blumer (1956) and by Dunning and Carlton (1956) allow a rather simple and positive separation of acidic and non-acidic porphyrins and are capable of determining the number of carboxylic groups per molecule. The paper pulp method of Dunning and Carlton (1956) is capable of reduction to a fairly routine procedure. As discussed under the section on spectra, infrared studies are useful for detecting the presence of the carbonyl group. The low temperature history indicated by observations of carboxylated porphyrins in bituminous materials is in harmony with recent theories on the origin of petroleum, so ably reviewed by Stevens (1956).

Porphyrin studies offer considerable support for the current theories that petroleum is formed slowly in marine or brackish environments from marine and terrestrial plant and animal matter and that the asphaltic constituents of crude oils are of primary formation. During the evolution of the oil these simplify to form the clean, paraffinic oils commonly associated with older formations.

Although much remains to be learned concerning the occurrence and implications of porphyrins in bituminous materials, porphyrin studies have reached a stage where the results form a consistent and logical pattern. Needless to say, the consistency and logical arrangement of even a large amount of data does not insure the absolute correctness of the conclusions.

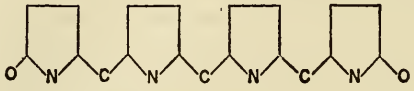
Other Pigments

The geochemical importance of porphyrins and their stable metal complexes has been established by the numerous investigations discussed above. These pigments are particularly adapted as tracers for some of the processes involved in the formation, migration, and accumulation of petroleum and other bituminous materials. However, other types of natural coloring matters also may prove to be of value for the development of additional geochemical correlations. Some examples of such pigments will be reviewed briefly together with possible applications of their physical and chemical properties for studies of bitumens. An extensive discussion of the many types of natural pigments is beyond the scope of this chapter. For more complete information, reference should be made to the reviews and general articles listed in the bibliography.

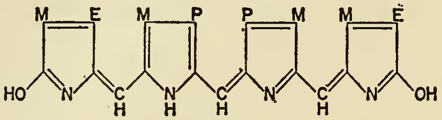
Bile Pigments—The occurrence, chemical and physical properties, and methods of isolation of the bile pigments have been reviewed by Lemberg (1938) and treated in detail by Lemberg and Legge (1949). The bile pigments have been known to medical and clinical scientists for many years. Their instability and occurrence in complex mixtures has resulted in rather complicated systems of nomenclature and designation. Lemberg (1938, 1949) developed a logical and systematic treatment of these substances that will be used in the following discussion. The occurrence of these pigments in forms of life that may be of geochemical interest also is reviewed in the volumes of Rabinowitch (1945, 1951).

The bile pigments are primarily of clinical interest and accordingly have been studied extensively from that viewpoint. However, they also are of geochemical interest because of their close relationship to the porphyrins and hematins and because they occur as the coloring matter of several species of algae. The basic structural unit and examples of typical bile pigments are shown in Figure 11, according to the treatment of Lemberg and Legge (1949).

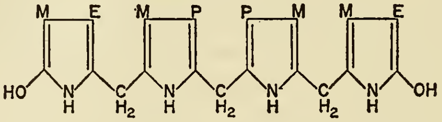
Many of the interesting properties of the porphyrins are caused by the stable resonance structure of the closed ring. The open system of the bile pigments has a much lower resonance effect and lower stability than the porphyrins and these pigments would be expected to occur in bituminous materials less commonly, if they occur at all, than do the porphyrins. The open chain tetrapyrrolic pigments are typified by numerous stages of dehydrogenation ranging from the aromatic biliverdins to the fully hydrogenated bilirubinogens (Fig. 11). Each of the dehydrogenation stages has a typical color, absorption spectrum, and chemical properties. Lemberg and Legge (1949) report that, with few exceptions, only compounds with side chains consisting of 4 methyl, 2 vinyl, and 2 propionic acid groups or of 4 methyl, 2 ethyl, and 2 propionic acid side chains have been observed in nature. Furthermore, these side chains are arranged only as are those of the type IX porphyrins.



Bile pigment nucleus



Mesobiliverdin



Mesobilirubinogen

FIG. 11. Structures of bile pigments (group symbols: M = methyl, E = ethyl, and P = propionic acid).

The verdins, violins, erythrins, and rubins range in color from blue through violet to orange and contain 10, 8, 7, and 5 conjugated double bonds, respectively. The more completely hydrogenated forms, mesobilene and mesobilirubinogen, contain 5 and 2 conjugated double bonds, respectively, and are yellow or colorless. This range of coloration, reflecting a shifting of the absorption bands to shorter wavelengths with decreasing conjugation, follows the general theories of light absorption by chromophores and will be discussed under the carotenoids.

The chemistry of the bile pigments has been systematized as the result of much research by several workers until the several types and variations now form a relatively consistent picture. The main types of bile pigments and their absorption spectra are summarized in Table 12, according to the data of Lemberg and Legge (1949).

Many of the bile pigments have absorption bands in the ultraviolet region and early studies were performed with instruments capable of

Table 12.

Absorption Spectra of some Bile Pigments

Lemberg and Legge (1949)

Type	Example	Color (neutral)	Absorption spectra		
			Pigment		Zinc salt*
			Maxima, mμ	Solvent	Maxima, mμ
Bilatrienes	Biliverdin	Blue-green	680 377	$HCl-CH_3OH$	—
(verdins)	Biliverdin		640 392	CH_3OH	—
	Mesobiliverdin		670 363	$HCl-CH_3OH$	685
Biladienes (a,b)	Mesobiliviolin	Red	570 —	$CHCl_3$	625 575
(violins)	Mesobiliviolin		607 —	$HCl-CHCl_3$	—
(Erythrins)	Mesobilierythrin		560 495	5% HCl	630 509
Biladienes (a,c)	Bilirubin	Orange	450 —	$CHCl_3$	—
(rubins)	Mesobilirubin		425 —	$CHCl_3$	—
Bilenes (b)	Mesobilene (urobilin)	Yellow	452 330	Dioxane	509
			490 375	$HCl-CH_3OH$	—
Tetrahydro-bilene	Stercobilin	Yellow	456 322	Dioxane	506
			488 372	$HCl-CH_3OH$	—

* In methanol.

observing spectra only in the visible region. In addition, the use of a simple spectroscope is more convenient than that of instruments such as the spectrophotometer which is capable of recording ultraviolet spectra. It is, therefore, common practice to prepare the zinc complexes of these pigments, many of which have absorption bands in the visible region (Table 12). The fluorescence, or lack of fluorescence, of these zinc complexes under ultraviolet light is a key to their identity. For example, among the biladienes the violins form zinc salts that are blue-green and have red fluorescence, and the zinc salts of the rhodins are red and have a yellow fluorescence.

Examples of common bile pigment tests will be discussed but briefly; the comprehensive treatise of Lemberg and Legge (1949) is recommended for additional details, methods, and applications of such methods. The bile pigments, in addition to their spectral properties and zinc salts, are commonly identified by the Gmelin reaction. Although this reaction is only partly understood, it has been of considerable value in bile pigment studies and is based on the color changes which occur when the pigments are treated with nitric acid containing nitrous acid. A favored clinical method at present seems to be the method of Van Den Bergh in which bilirubin is coupled with diazotized sulfanilic acid to form a dye which can be determined colorimetrically with fair accuracy.

Small amounts of the bilatrienes may be identified by dissolving them in ammoniacal alcohol and adding small amounts of zinc acetate with iodine. The result is a zinc complex salt of a biliviolin type which has a green color, an absorption band at 625 or 635 mμ, and intense red fluorescence The rubins may be dehydrogenated by ferric chloride, nitric acid, benzoquinone, and other oxidizing agents. These reactions lead to other forms of the bile pigments which may then be used as derivatives for the identification of the original compound. These reactions are discussed in detail by Lemberg and Legge (1949) and by Siedel and Frowis (1940) who studied the complex mechanisms involved.

A recent article by Zak and associates (1954) demonstrates the application of color changes, as a result of oxidation by various reagents such as sulfuric acid containing glacial acetic acid or ferric chloride, for the estimation of bilirubin. The quantitative method used is a good example of recent analytical methods based on spectrophotometric comparisons.

The hydrochloric acid method of Willstatter and associates (1913a, 1913b), so useful for porphyrin studies, was first applied to bile pigments by Lemberg (1930a) and was shown to be generally useful for the more strongly basic types. As in the related phases of porphyrin research, common procedures for isolating and characterizing the bile pigments include adsorption and partition chromatography, distribution between immiscible solvents, and solvent extraction.

Although the common forms of bile pigments contain four pyrrole groups, dipyrrolic substances also occur naturally. Among these are bilifuscin and pentdyopent. The structures of these substances are shown in Fig. 12.

Porphobilinogen, a biosynthetic precursor of porphyrins and hematins, was shown to be a monopyrrole by Cookson and Rimington (1953). This substance also is of interest because Waldenstrom and Vahlquist (1939) showed that it is readily converted to uroporphyrin by the action of acid. Two bacterial pigments also are of interest. These are prodigiosin, a red pigment that has been shown by Wrede and Rothhass (1933) to consist of three pyrrole groups linked to a carbon atom (Fig. 12), and violacein which, according to the studies of Tobie (1936), may be a pyrrolic pigment.

The work of Lemberg (1935) shows that bile pigments are formed in the degradation of hemin, however, Lemberg and Legge (1949, p. 471) report that they are not formed from the free porphyrins. The bile pigments are primarily related to the metabolic processes of animals. They are, therefore, common in the bile and faeces of many types, but certain of these substances have also been observed as the prosthetic groups of algal chromoproteins. Lemberg and Legge (1949) report that biliverdin occurs in the blue-green pigment of egg shells and in marine worms, but other bile pigments occur in the larvae of the bloodworm, in annelids, crustaceans, molluscs, and insects.

Two of the more geochemically interesting types of these pigments are phycocyanin and phycoerythrin, the chromoproteins of blue-green and red algae. The colored portions of these materials were called "phycobilins" by Lemberg (1929, 1930a), who first succeeded in splitting the protein portion from the bile pigments. The specific names of these prosthetic groups are phycocyanobilin and phycoerythrobilin, sometimes called cyanobilin and erythrobilin. The nature of these prosthetic groups as bile pigments and their identity with mesobiliviolin and mesobilierythrin also

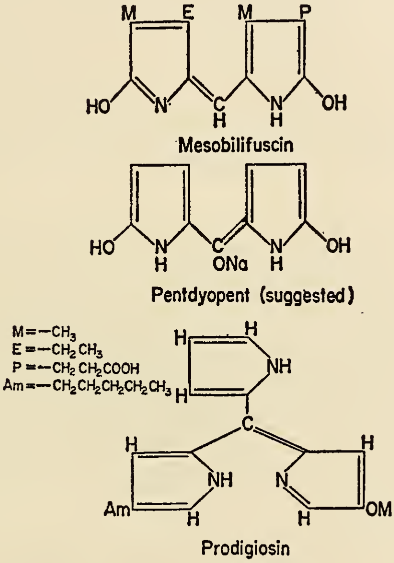


FIG. 12. Structures of pyrrolic pigments occurring in nature (Lemberg and Legge, 1949).

was established by Lemberg (1929. 1930a). Phycocyanin is a water-soluble blue pigment common in blue-green algae while phycoerythrin is the corresponding pigment of red algae. The occurrence of the phycobilins is commonest in certain classes of algae but, according to Lemberg and Legge (1949), they also appear in fishes, sponges, and bacteria and have been identified in flagellates and a blue diatom. The phycochromoproteins are water-soluble because of their high protein content; the chromophoric constituents, however, are typical of the bile pigments and are soluble in chloroform or alcohol but not in water. These chromoproteins, because of their intense colors, are particularly suited for sedimentation studies and were investigated extensively by Svedberg and associates (1928, 1932) in his ultracentrifuge. The results showed that the protein constituents were large, having molecular weights of about 208,000, and also gave interesting evidence of the effect of acids in splitting the protein portions.

The absorption spectra of the phycochromoproteins have been widely studied. Svedberg and associates (1928, 1932) reported that the phycoerythrins from various algae have absorption bands (in buffered aqueous solutions) at about 566, 540, and 498 mμ in the visible region, and at 260 and 360 mμ in the ultraviolet. Phycocyanin has absorption bands at about 615, 553, 360, and 260 mμ. These workers observed that the exact locations of these bands differed from species to species, perhaps because of differences in the attached proteins. Few data are available on the spectra of the free chromophoric groups, but Lemberg (1930b) reported that in concentrated hydrochloric acid cyanobilin and erythrobilin have peaks at 598 and 498 mμ, respectively.

Rabinowitch (1951) discussed the strong fluorescence of the phycochromoproteins in living cells and in extracts under ultraviolet light. The main fluorescence band of phycoerythrin is at 566 mμ and that of phycocyanin at 660 mμ. This strong fluorescence is an additional means for identification.

Detailed studies have shown that these pigments are present in both the red and the blue-green algae. Their chemical relationship as oxidized and reduced forms of similar compounds or as isomers has not been fully established. According to Kylin (1931), species of algae which live fairly deep in the sea contain only phycoerythrin and hence are bright red. Those living near the surface also contain phycocyanin and are brown, purple, or violet. Therefore, it appears that these pigments, or their degradation products, may prove of geochemical interest as a possible means of establishing rough estimates of the depths at which specific sediments accumulated.

Carotenoids—The carotenoids comprise many pigments which are widely distributed in plants and animals and are named after the most common and best known member of the class, carotene. Their structures consist mainly of long hydrocarbon chains forming an uninterrupted system of conjugated double bonds; hence they are known as the "polyene" pigments. This conjugated system causes the characteristic colors of the carotenoids which range from bright yellow, through red, to purple and deep blue. They often are referred to as "lipochromes" because of their general solubility in hydrocarbons or fats.

These natural pigments have been known to chemists over a century and have been studied continuously during that time. As a result, a vast amount of information on the numerous types has been accumulated. Many of the pertinent results are described in the monograph of Mayer and Cook (1943), the reviews of Karrer and Jucker (1950) Goodwin (1952), Bogert (1938), the volumes of Rabinowitch (1945, 1951) and the early treatise of Willstatter and Stoll (1928). Frequent reference will be made to these works because much of the original literature is in obscure German publications.

The nomenclature of these pigments was systematized by Bogert (1938). According to the system he suggests, the carotenoids containing only carbon and hydrogen are referred to as "carotenes" while those containing hydroxyl groups are referred to as "carotenols". Although the usage of Bogert has been adopted in some instances, specific pigments of this type commonly have retained their common names which end in "in" regardless of their composition.

Carotene, first identified in 1831, has at least three structural isomers, α-, β-, γ-carotenes of which β-carotene is the dominant form. These isomers occur in various ratios and, according to Mayer and Cook (1943), the average composition of carotene preparations is about 15%, 85%, and 0.1% α-, β-, and γ-carotene, respectively. The structure of β-carotene is shown in Fig. 13.

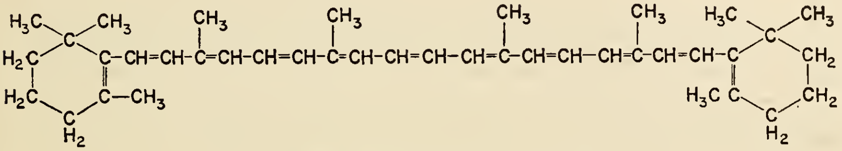


FIG. 13. The structure of β-carotene.

In α-carotene, the double bond of one ring is displaced so that the conjugated system is shortened. Other carotenes have one or both rings opened and have one or two additional double bonds. The substances are biologically interesting because hydrolysis of the central double bond produces Vitamin A.

The carotenols are more diversified than the carotenes. Several groups occur, containing one to six oxygen atoms and having several isomeric forms. Common examples are the xanthophylls, comprising a mixture of pigments, the most plentiful of which is lutein, or, more properly, luteol. The xanthophylls have been so extensively studied that many workers prefer to retain this name to describe a group of carotenols containing forty carbon atoms. The unfortunate similarity of this name to chlorophyll, despite the dissimilarity of structure, results from the pioneering work of Berzelius who originally thought that the yellow pigment of leaves, which he called xanthophyll, was a decomposition product of chlorophyll.

Carotenoids are found in practically all types of plants, from the simplest to the most complex, and may be present in almost any part of the plant. They seldom occur singly and, according to Bogert (1938), at least five of these pigments are found in purple bacteria. The carotenoids generally are insoluble in water and hence are not found in cell fluids. The notable exception is crocin, the main constituent of the saffron pigment which consists of a glycoside (sugar complex) of crocetin. Mayer and Cook (1943) report that in addition to their occurrence in green plants, carotenols have been found in yellow leaves, fruit rinds, the cocoon of the silkworm, and in the feces of cattle and sheep. Zechmeister (1950) and Bogert (1938) present long lists of the occurrence of these substances in varied forms of plant and animal life. Lycopene, other carotenes, and the carotenols are frequently encountered in animals. A few of these are peculiar to animals, such as retinene, violerythrin, and astacin. It appears that vertebrates generally are incapable of synthesizing the carotenoids; those which they contain usually are ingested plant types. On the other hand, invertebrates either synthesize or transform carotenoids since Bogert (1938) reports that they contain types unknown in plants. Lemberg (1938) reports that the carotenes are selectively taken up by some animals such as the horse and cow, carotenols by birds, and both types of substances by man. Rhodopsin, a carotenoid-albumin, is an important factor in the visual cycle of animals, birds, amphibians, and some marine fishes.

Perhaps of more geochemical interest, Rabinowitch (1945) states that all known algae contain carotenes and most contain carotenols. In addition, they contain several carotenols not found in higher types of plants. The most important of these pigments, fucoxanthol, is found mainly in brown algae and diatoms. The formula of this substance is not precisely known, but Heilbron and Phipers (1935) lists it as $C_{40}H_{60}O_6$. Aside from the additional hydroxyl and carbonyl groups, it differs from β-carotene in that the terminal "rings" are not closed. This substance has been found in green and red algae while blue-green algae contain at least two carotenoids unknown in higher plants. In addition, the review of Bogert (1938) shows that most orange- colored bacteria contain carotenes.

Certain of the carotenes are common in marine invertebrates. Actinoerythrin, as a protein complex, comprises from 70 to 80% of the carotenoids in one species, while astaxanthin ($C_{40}H_{52}O_4$) and echinone ($C_{40}H_{58}O$) make up about 60% in another according to De Nicola and Goodwin (1954). Six other pigments are reported to occur in small amounts in these invertebrates, four related to carotene and two related to echinone. Fucoxanthol and violaxanthol ($C_{40}H_{56}O_4$) have both been observed in brown algae. Rabinowitch reports that purple bacteria contain rhodoviolascin ($C_{42}H_{60}O_2$), rhodopol ($C_{40}H_{58}O$) and flavorhodin; the diatoms contain derivatives of fucoxanthol; and the dinoflagellates contain peredinol.

The carotenoids have not been identified in bituminous materials. This may well be because, although of a conjugated and hence resonant system, their stability must be considered several orders lower than that of the porphyrins. Even if originally present, they may have degraded to simpler forms in the course of geological time. Many of the carotenoids are sensitive to heat and light and other forms of radiant energy, and are extremely sensitive to oxidation. In addition, they are subject to reduction. An important consideration, were they to be expected to withstand aging in petroleum-producing formations is the fact that, unlike the porphyrins, they do not form stable metal complexes which appear to be a vital factor in the survival of porphyrins in bituminous materials. It is, of course, entirely possible that the carotenoids exist in bituminous materials. If so, their identities would be more difficult to establish than those of the porphyrins which have distinctive spectra as discussed above. However, the rarity of olefins in crude oils is an argument against the possible occurrence of these substances in such materials. Some petroleum constituents may have been produced by carotenoid degradation, but no case has been proved.

Lochte and Littman (1955), in reviewing the occurrence of acids in petroleum, report the isolation of 2, 2, 6-trimethylcyclohexanecarboxylic acid. The occurrence of this acid is at least philosophically interesting because examination of the structural formula of β-carotene shows that the end groups are of the 2, 2, 6-trimethylcyclohexane structure and would require only hydrogenation of a double bond and oxidation of the carotene chain to form this acid. This particular acid is listed only as an example, and it would be extremely difficult to establish the validity of this relationship. However, an examination of the structural components of the common natural pigments reveals that they could possibly account for many of the complex minor constituents of petroleum.

Although carotenoids have not been isolated from petroleum and related materials, extensive studies have been made of their occurrence in marine and fresh-water sediments. Trask and Wu (1930) first reported the presence of carotenoids in lake sediments. In a period of a few years following this report, carotenes and carotenols were detected in lake and marsh sediments. Many of the early results are summarized by Vallentyne (1956, 1957a) who concludes that, unlike the sedimentary chlorophyll degradation products, most of the carotenoids appear to be the unchanged constituents of the organisms that produced them.

Lederer (1938) isolated crystalline carotene, myxoxanthin, two xanthophylls, and eleven other unidentified carotenoids from a lake sediment. Karrer and Koenig (1940) reported that rhodoviolascin, a pigment common to purple bacteria, was the main carotenoid in sediments of Lake Nakuru, Africa. Vallentyne (1956) found α- and β-carotenes in lake sediments estimated to be 11,000 years old by radiocarbon dating.

About twenty different carotenoids have been detected in sediments. However, as Vallentyne (1957a) emphasizes, only β-carotene α-carotene, and rhodoviolascin have been absolutely identified. Vallentyne (1957b) identified β-carotene in California lake sediments which were about 20,000 year old, reported (1957a) that the oldest sediments shown to contain carotenoids are interglacial types in Denmark estimated to be 100,000 years old, and that carotenoids have not been observed in lithified sediments.

Fox (1937) identified α- and β-carotenes in marine sediments and reported the presence of pigments similar to rhodopurpurin and perhaps astacene. Fox and associates (1941, 1944) tentatively identified other pigments of carotenoid types in sediments. The types observed are common in the sea anemone, purple bacteria, and crustaceans, and were identified by means of spectral studies and chromatography.

Vallentyne (1956) concluded that there is little difference between carotenoids of marine or fresh water sediments that cannot be directly attributed to the different types of plant remains found in these sediments. These pigments are not necessarily as old as the sediments from which they are isolated because of the possibility of their synthesis by micro-organisms in the sediments. Furthermore, the relationship of recent sediments to petroleum formation is not understood. However, the large amount of geochemical work on recent sediments, and the occurrence of natural pigments in these sediments, indicates the geochemical value of research on such pigments.

The studies of Vallentyne (1956) and Fox and associates (1941, 1944) are excellent examples of the applicability of adsorbent and partition chromatography coupled with spectral studies and physico-chemical tests for the identification of pigments present in complex materials in only very small amounts. The spectral identity of β-carotene from a lake sediment and pure β-carotene is shown in Fig. 14 which is reproduced from unpublished data of Vallentyne.

Because the carotenoids are yet to be identified in petroleum and related materials, only a brief discussion of their properties, identification, and isolation will be made. Like the porphyrins, the carotenoids are most readily recognized by their absorption spectra which generally have a major peak and one or two minor peaks in the visible region. The spectral properties of some typical examples of these substances are summarized in Table 13.

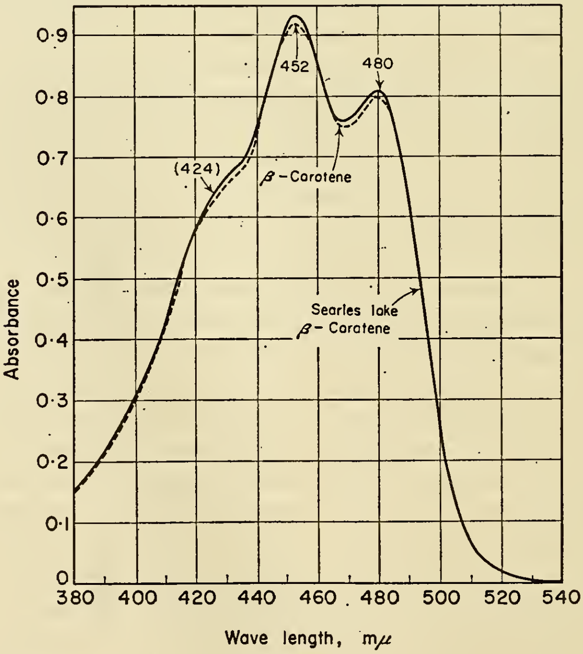


FIG. 14. Comparison of absorption spectra of pure β-carotene with β-carotene isolated from Searles Lake sediment (Vallentyne, unpublished).

TABLE 13.

Absorption Spectra, Composition, and Occurrence of Carotenoids

Carotenoid	Formula	Occurrence	Absorption bands, mμ							
			Carbon disulfide				Petroleum ether			
			I	II	III	Ref*	I	II	III	Ref*
Carotenes:										
α-Carotene	$C_{40}H_{56}$	Most plants	509	477	—	F	478	448	423	M
β-Carotene	$C_{40}H_{56}$	Most plants	520	485	450	F	484	452	426	F
γ-Carotene	$C_{40}H_{56}$	Most plants	534	496	463	F	495	462	431	M
Lycopene	$C_{40}H_{56}$	Fruits	548	508	477	F	506	478	447	F
Rhodopurpurin	$C_{40}H_{56}$	Pur. bact.	550	511	479	B	—	—	—	
Carotenols, One hydroxyl group.†										
Kryptoxanthin	$C_{40}H_{56}O$	Berries	519	483	452	F	485	452	424	M
Lycoxanthin	$C_{40}H_{56}O$	Fungus, tom.	547	507	473	F	503	472	443	M
Rhodopol	$C_{40}H_{56}O$	Pur. bact.	547	508	478	M	—	—	—	
Rubixanthin	$C_{40}H_{56}O$	Roses	533	494	461	F	495	463	432	M
Two hydroxyl groups:										
Luteol	$C_{40}H_{56}O_2$	Most plants	506	474	440	R	477	447	—	M
Rhodoviolascin	$C_{42}H_{60}O_2$	Pur. bact.	573	534	496	B	—	—	—	
Zeaxanthin	$C_{40}H_{56}O_2$	Corn	517	482	450	F	484	452	423	F
Three hydroxyl groups:										
Antheraxanthin	$C_{40}H_{56}O_3$	Tiger lily	510	478	445	F	—	—	—	
Flavoxanthin	$C_{40}H_{56}O_3$	Buttercup	478	448	420	B	450	422	—	M
Four hydroxyl groups:										
Taraxanthin	$C_{40}H_{56}O_4$	Flowers	501	469	440	B	472	443	—	M
Violaxanthin	$C_{40}H_{56}O_4$	Oranges	500	469	440	F	472	443	418	F
Ketones										
Myxoxanthin	$C_{40}H_{54}O$	Blue-green algae	—	488	—	B	—	—	—	
Rhodoxanthin	$C_{40}H_{50}O_2$	Tree leaves	564	525	491	B	524	489	458	M
Hydroxy carbonyl compounds:										
Fucoxanthin	$C_{40}H_{60}O_6$	Brown algae	510	477	445	B	478	451	423	R
Carboxylic compounds:										
Crocetin	$C_{20}H_{24}O_4$	Saffron	482	453	—	B	—	—	—	
Azafrin	$C_{27}H_{38}O_4$	Plant root	476	446	419	M	—	—	—	

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* References: B = Bogert (1938), F = Frye (1951), M = Mayer and Cook (1943), R = Rabinowitch (1951).

† According to modern nomenclature, all hydroxyl-containing carotenoids should end in "ol"; common names retained to avoid confusion.

As shown in Table 13, the absorption bands of the bacterial carotenoids are located at longer wave lengths than those of green plants, paralleling the relationship between bacteriochlorophyll (of bacteria) and chlorophyll (of green plants).

The carotenoids commonly have been identified by their typical color reactions, resistance to alcoholic alkali, partition between immiscible solvents, and elementary analysis as used originally by Willstatter and Mieg (1907). The usefulness of such tests is extremely limited for their identification in bituminous extracts. Such materials, if present at all, would be in small amounts, hence, extracts containing them would contain small amounts in high dilution. This factor alone would eliminate most of the above methods. Furthermore, the difficulty of observing any typical chemical or group reaction in bituminous extracts is well known. Because the carotenes are hydrocarbons, their separation would be very difficult and accordingly inefficient. The carotenols would be more readily isolated because of their hydroxyl groups. Methods such as those used for carotenes in sediments by Vallentyne (1956) offer most promise.

Two of the standard color tests are reactions with sulfuric acid and with antimony trichloride. The carotenoids, in relatively pure forms, give dark blue, violet, or greenish-blue colors when treated with concentrated sulfuric acid. When they are brought into contact with an anhydrous chloroform solution of antimony trichloride, a deep blue color is formed. Concentrated hydrochloric acid with some phenol also gives a dark blue color with carotenoids. These, and other, tests are discussed in detail by Bogert (1938). The carotenoids are well known for their ready crystallization. However, in the complex extracts of bituminous materials it is likely that there usually would be sufficient impurities to obviate this type of separation.

Mayer and Cook (1943) report that the carotenoids have considerable optical activity, a property that may prove useful in their identification. However, the development of rapid and precise spectrophotometers causes spectral absorption investigations to be most promising. For this reason, the absorption maxima of several pigments of this class were tabulated above (Table 13). The spectra of pure lycopene and β-carotene are shown in Fig. 15 according to Zechmeister and associates (1943). Comparison of these spectra with the spectra of porphyrins shown elsewhere indicates the difficulties that will be encountered in making identifications from spectra of carotenoid-rich extracts. Whereas the porphyrins have four strong peaks in the visible region, and one very strong peak in the ultraviolet region, the peaks of the carotenoid spectra are superimposed on a large, broad absorbance "hump". According to Fieser (1950) a typical carotenoid, containing ten or eleven conjugated double bonds, has a three-banded spectrum in which the band of greatest intensity is halfway between the other two bands. This spectrum represents the peak of a broad absorption band differing from systems with two or three conjugated double bonds in having fine detail in the form of "shoulders" which are developed into the two companion bands. From theoretical and empirical correlations, Fieser (1950) was able to develop an equation for calculating the position of the main band of a carotenoid from its structure. The spectra of some common carotenoids reproduced below (Fig. 15) illustrate these comments. This type of spectrum would be definitive for the identification of these substances only in relatively pure solutions.

The effects of solvents on the absorption spectra of the carotenoids are quite strong. For example, the two main peaks of β-carotene are located about 20 mμ further toward the red in carbon disulfide than in solutions in hydrocarbons or alcohols. According to Fieser (1950), the sensitivity to solvent effects increases with the length of the conjugated system which the carotenoid contains. The effects of solvents on the locations of the absorption bands of some common carotenoids are summarized in Table 14, mainly from the data of Frye (1951) and the review of Rabinowitch (1951).

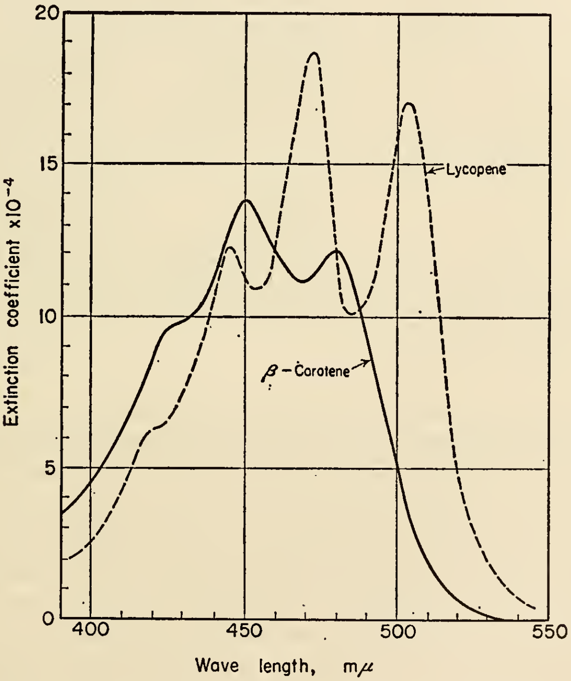


Fig. 15. Absorption spectra of lycopene and β-carotene in hexane (Zechmeister and associates, 1943).

The individual carotenoids usually are isolated from plant extracts by partition between immiscible solvents, saponification with alcoholic alkali, and chromatographic methods. Many modifications of these basic methods are based on the original work of Willstätter and Stoll (1913). Recently, White and Zschiele (1942) determined the partition coefficients

TABLE 14.

Absorption Spectra of Carotenoids in Various Solvents

Carotenoid	Formula	Solvent	Absorption Bands, mμ I	II	III	Ref.*
β-Carotene	$C_{40}H_{56}$	Hexane	482	451	—	F
		Petroleum Ether	484	452	426	F
		Ethyl Ether	478	449	—	R
		Chloroform	497	466	—	F
		Carbon Disulfide	520	485	450	F
Lycopene	$C_{40}H_{56}$	Petroleum Ether	506	478	447	F
		Ethanol	503	472	443	F
		Chloroform	517	480	453	F
		Benzene	522	487	455	F
		Carbon Disulfide	548	508	477	F
Luteol	$C_{40}H_{56}O_2$	Petroleum Ether	477	447	—	M
		Ethyl Ether	472	447	420	R
		Chloroform	485	457	430	R
		Carbon Disulfide	506	474	440	R
Fucoxanthol	$C_{40}H_{56}O_6$	Hexane	477	451	—	R
		Ethanol	492	457	—	R
		Chloroform	484	459	—	R
		Carbon Disulfide	510	477	445	B

* References: B = Bogert (1938), F = Frye (1951), M = Mayer and Cook (1943), R = Rabinowitch (1951).

of pure β-carotene ($C_{40}H_{56}$), kryptoxanthol ($C_{40}H_{56}O$), and zeaxanthol ($C_{40}H_{56}O_2$) between hexane and aqueous solutions of methanol and other alcohols. These studies showed that any two of these carotenoids could be readily separated by partition but that only fair results were obtained if all three were present. Zschiele and Porter (1945) developed general spectrophotometric methods for the quantitative determination of several of the common carotenoids. These methods, which involve measurements of light absorption at selected wave lengths, are precise, rapid, and not overly demanding in instrumentation. The development of a spectrophotometer for carotenoid studies is described in the work of Smith (1936). These studies showed that earlier methods using spectroscopes often resulted in the inaccurate location of absorption bands, probably because they were unsymmetrical. Today, most spectral work is carried out with commercial spectrophotometers, either single-beam manual types or the more expensive double-beam direct-recording types. For this reason, the recent literature contains considerably fewer conflicts regarding spectral data.

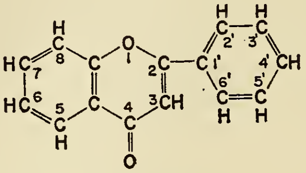
The adsorption of the carotenoids, on which their chromatographic separation is based, is dependent on their structure. Thus the carotenes, being hydrocarbons, are weakly adsorbed on polar adsorbents while the adsorption of the carotenols increases with their hydroxyl content. The adsorption of ketonic and carboxylic carotenoids also would depend on the numbers and locations of polar groups. It is interesting to note that Tswett (1903) originally developed the chromatographic method for the separation of leaf pigments. This is regarded by many specialists as the most valuable contribution to the physical chemistry of the carotenoids since the introduction of spectroscopy. The recent emphasis on separation of natural and synthetic substances indicates that this importance is common also to most fields of analytical organic chemistry. By the use of proper adsorbents and eluents, Tswett (1903) was able to isolate "pure carotene" which had light absorption peaks at the positions listed many years later by Smith (1936) and other workers.

Although the chromatographic method was developed about 1900, its value as a preparative method was not fully realized until the work of Kuhn and Lederer (1932) on the carotenoids. Such methods were developed rapidly until in a few years Cook (1936) listed chromatography as the standard method for investigating the carotenoids. The importance of chromatography for such studies has been maintained and increased until modern texts on chromatography such as those of Strain (1942), Zechmeister (1950), and Lederer and Lederer (1955) commonly include a section on the carotenoids.

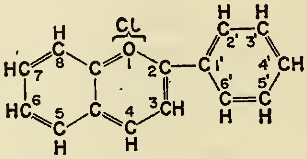
The development of definitive chromatographic and spectrophotometric methods affords excellent means for studying the carotenoids in sediments and for determining their value for geochemical studies of bituminous materials.

Flavones and Anthocyanins—The flavones are the most widely distributed natural pigments satisfactory for dyestuffs. Thus they are well known and have been studied extensively. Excellent reviews of the chemistry and occurrence of these pigments and the related anthocyanins have been published by Link (1943) and by Mayer and Cook (1943). These pigments occur mainly as glycosides (sugar complexes), associated with tannins, and sometimes in the free state. Most of the flavones are yellow solids, soluble in polar solvents and aqueous solutions. For this reason they are of less interest in petroleum geochemistry than are the lipochromes (oil-soluble pigments) such as the porphyrins and carotenoids. However, their decomposition products are stable organic acids and phenolic compounds similar to substances found in petroleum as discussed below.

The structure of flavone, the prototype of these pigments, is shown in Fig. 16. Flavonol is formed if the hydrogen atom of carbon (3) is replaced by a hydroxyl group; if the double bond between carbons (2) and (3) is reduced, the product is called "flavanone". The isoflavones have the phenyl group attached to carbon (3) instead of (2). The several pigments of these series differ in that one or more of the hydrogen atoms on either the phenyl or benzopyrone rings are substituted by hydroxyl groups. Reference should be made to the reviews listed above for descriptions of specific pigments. The structures of some common forms of the flavone pigments are summarized in Table 5, according to the system of Link (1943).



Flavone



Flavylium chloride

Fig. 16. Structures of flavone and anthocyanin pigments.

Table 15.

Structure and Occurrences of Common Flavones

Pigment	Occurrence	Positions of Hydroxyl Groups	
		Benzopyrone no.	Phenyl no.
Flavone	Flowers, leaves, seeds	—	—
Chrysin	Buds of trees	5,7	—
Apigenin	Parsley, dahlias	5,7	4′
Luteolin	Weld	5,7	3′,4′
Fisetin	Wood and quebracho	3,7	3′,4′
Galangin	Roots	3,5,7	—
Kaempferol	Blue delphinium, fruits	3,5,7	4′
Quercetin	Tree leaves, bark	3,5,7	3′,4′
Myricetin	Oriental evergreen	3,5,7	3′,4′,5′

The basic properties of the heterocyclic oxygen atom allow these pigments to form unstable oxonium salts with acids. The colors of these salts generally are brighter than those of their corresponding bases, a property that may be used for their identification. Wilson (1939) observed that the flavones, with the exception of fisetin, produced a brilliant yellow color with boric acid solutions. The flavanones do not give this reaction. This test, combined with the cyanidin test may, therefore be used as a qualitative test for flavanones.

The flavones form red, yellow, or orange precipitates when their solutions are treated with lead acetate. Several produce a bright yellow color when concentrated sulfuric acid is added to their glacial acetic acid solutions. Many of the typical flavone tests are described by Wolfrom and associates (1941) who used them to establish the presence of an isoflavone in the Osage Orange.

The flavones commonly are isolated by adsorption or partition chromatography. Ice and Wender (1952) studied the separation of two and three component mixtures of flavonoids on a Magnesol column. Gage and associates (1951) made an extensive study of the partition chromatography of some thirty-eight flavonoids. For these studies, the common strong yellow, red or orange fluorescence of the flavonoids, with or without added chemicals, is a valuable aid in their location and identification. These studies, and related ones, show that chromatography is an excellent tool for preparation, identification, and establishing the purity of the flavonoids.

Skarzynski (1939) reported that the flavones have two light-absorption bands between 290–380 mμ and 230–280 mμ, in the ultraviolet region. This absorption is due to the pyrone nucleus and therefore is general for this type of pigment. The 3-hydroxyflavones have a strong absorption band at 310 mμ and the other two bands are shifted to longer wave lengths. Spectral studies may be used to identify these pigments and to differentiate between closely related types; the paucity of spectral data in the literature is, therefore, surprising. However, these pigments generally have been isolated from flowers and other sources where they are present in relatively high concentrations and where there is a minimum of interfering substances. An increasing use of spectral data is evident. For example, Hasegawa (1952) in reporting studies of the flavonoids, lists spectral data for some specific types. Naringen, 5,7,4′-trihydroxyflavanone, has a weak absorption band at 312 mμ and a stronger band at 288 mμ; genkwanin, 5,4′-dihydroxy-7-methoxyflavone, has absorption peaks at 355 and 256 mμ. As mentioned above, the flavonoids fluoresce strongly under ultraviolet light; their fluorescence in boric acid solutions provides a method for their quantitative determination.

The anthocyanin pigments are represented in nature by the numerous shades of blue, purple, violet, and red colors of the flowers, fruits, leaves, and stems of plants. These pigments usually occur in the form of complexes with natural sugars. The sugar-free chromophoric groups are identified by the term "anthocyanidins". Much of the early research on these pigments was conducted by Willstatter and his associates (1914, 1924) who showed that the various colors of the anthocyanins resulted from relatively small changes in the basic structural unit, benzopyrylium chloride. The structure of the simplest pigment of this type, flavylium chloride, is shown in Fig. 16. The anthocyanins form salts with both acids and bases. The former are known as the "flavylium salts" and, unlike the flavone salts, are stable in aqueous solutions.

Extensive investigations have shown that there are six basic types of the anthocyanidins that are reviewed by Link (1943) and Robinson (1933). Each of these types has several derivatives many of which are described by Mayer and Cook (1943). The structures and occurrences of examples of these types are summarized in Table 16.

TABLE 16.
Structures and Occurrences of Anthocyanins

Pigment type	Occurrence of derivative	Position of hydroxyl or methoxyl groups	
		Hydroxyl	Methoxyl
Pelargonidin	Aster, strawberries	3,5,7,4′	—
Cyanidin	Roses, purple maize	3,5,7,3′,4′	—
Delphinidin	Gentians, vetches	3,5,7,3′,4′,5′	—
Peonidin	Cranberry, peony	3,5,7,4′	3′
Malvidin	Grape, sugar cane	3,5,7,4′	3′,5′
Hirsutidin	Flowers, red cabbage	3,5,4′	7,3′,5′

Link (1943) reports that the anthocyanins contain natural sugars attached to one or more of the hydroxyl groups; the most widely distributed form is the 3,5–diglucoside. Some of the anthocyanins in addition to the sugar molecules also contain organic acids attached to the hydroxyl groups of the pigment or to an hydroxyl group of the sugar with which they are complexed. The anthocyanidins usually are isolated by an initial extraction of the plant material with acidic or neutral alcohol from which the pigments are precipitated by adding ethyl ether. The pigment then is redissolved in aqueous HCl and recrystallized by adding alcohol and ether. Final purification is often obtained by chromatographic methods such as those of Spaeth and Rosenblatt (1950), which involve partition on silicic acid.

Many forms of the anthocyanins have been isolated from flowers and fruits in which they usually occur as mixtures. According to Link (1943), the petals of certain species are notably rich in anthocyanins; the dark blue pansy has an anthocyanin content of about 30%. The pigments generally are purple in neutral solutions, the acid salts are red, and the basic salts blue. Interestingly enough, Erikson and Robinson (1938) reported that no anthocyanins had been observed in micro-organisms.

The work of Robinson (1933) is outstanding for the detection of the anthocyanins. The methods used were primarily color tests depending on the color changes occurring when the plant extracts were reacted with alkalis and ferric chloride. For example, petunidin and delphinidin are rapidly destroyed by aqueous solutions of sodium hydroxide while the other types are relatively stable. Robinson (1933) also characterized the anthocyanins by their partition between immiscible solvents. For example, in a system containing 1% HCl solution, anisole, and ethylisoamyl ether, delphinidin is not extracted from the acid, small amounts of petunidin are extracted, cyanidin is extracted to a considerable extent and malvidin, peonidin, and pelargonidin are completely extracted. These methods are discussed in detail in the review by Link (1943).

The anthocyanins and anthocyanidins have pronounced light absorption in the visible and ultraviolet regions. All members studied by Link (1943) have a strong absorption band at about 270 mμ (ultraviolet). The chlorides of pelargonidin, cyanidin, and delphinidin have a strong peak from 510 to 550 mμ, and pelargonidin has weaker peaks at about 450, 400, and 330 mμ. Spaeth and Rosenblatt (1950) reported that the replacement of one or more hydroxyl groups on the phenyl ring causes a small displacement of the visible peak toward longer wave lengths. Thus, the locations of the visible peak for delphinidin (no methoxyl), petunidin (1 methoxyl), and malvidin (2 methoxyl) are at 547, 549, and 551 mμ, respectively. According to Sondheimer and Kertesz (1948), the anthocyanin pigment of strawberries has an absorption peak at 500 mμ and a weak one at about 480 mμ. It appears that the anthocyanin types may be recognized generally by their visible and ultraviolet spectra, and that infrared studies should be capable of discerning some of the finer details of their structure. Because their fission products are stable, well known products, classical chemical experiments have proved very useful in elucidating their structures.

Although the flavones and anthocyanins have not been isolated from bituminous substances, and apparently not from sediments, several of their decomposition products, among which are phloroglucinol, salicylic acid and benzoic acid (Fig. 17), may prove to be of geochemical interest. Certain of the products of hydrolysis or reaction of the flavones and anthocyanins are rather unusual and exceedingly stable. Whether or not they possess the unique qualities which characterize the porphyrins, and which permit the geochemical correlations discussed above, remains to be determined.

Link (1943) reports that the flavones and anthocyanins decompose to phloroglucinol and hydroxybenzoic acids such as salicylic and pyrocatechuic acids. The fact that this type of decomposition may be accomplished in the laboratory is no assurance that it occurs in bitumen-producing formations. However, many of these products are sufficiently stable that a very low reaction rate constant would produce detectable amounts during geologic ages. Although phloroglucinol has not been specifically identified in petroleum, several cresols, xylenol, phenols, and naphthol have been reported by von Braun (1938) and by Hancock and Lochte (1939). Structures of some of these compounds are shown in Fig. 18.

The work of Lochte and associates at the University of Texas is of particular interest in this regard. The summary of this work, and a review of the subject, recently has been prepared by Lochte and Littman (1955). This review is a fascinating account of the unusual difficulties and accomplishments accompanying work on the petroleum acids. According to Lochte and Littman (1955), many petroleum samples contain acids having aliphatic chains, cyclohexane rings, cyclopentane rings, and aromatic rings, as well as phenols, cresols, and xylenols. The most common type of naphthenic acids (a term by which von Braun (1938) described the petroleum acids) apparently are monocyclic types. However, bicyclic and aliphatic types also are common. Extremely low concentrations and difficult separations have limited the knowledge of the higher molecular weight petroleum acids and oxygenated compounds. Reference should be made to the reviews of von Braun (1938) and Lochte and Littman (1955) for details of separation and identification.

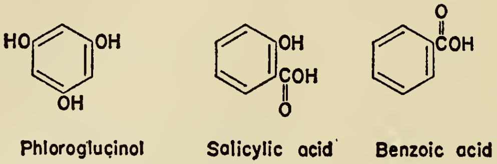


FIG. 17. Decomposition products of flavones and anthocyanins.

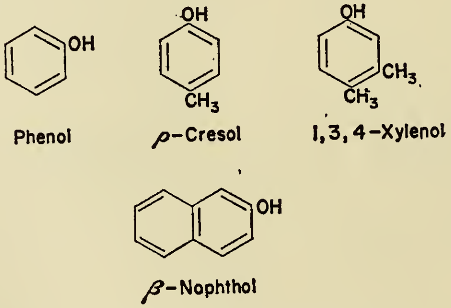


FIG. 18. Structures of some substances isolated from petroleum.

Although the known compounds are not so directly related to their original forms as the porphyrins (for example) and sometimes may be artifacts of some of the methods used, modern methods of isolation and identification give promise of considerable progress in this interesting problem.

Miscellaneous pigments—In addition to the types of pigments discussed above, several less common types have characteristic structures that may prove useful in geochemical studies. The chemical formulas and occurrence of some pigments having common chemicals as their basic ring structures are summarized in Table 17.

Table 17.

Constitution and Occurrence of Miscellaneous Pigments

According to Mayer and Cook (1943)

	Chemical formula	Common name	Occurrence
Hydrocarbon ring structure			
Benzene	2, 6-dimethoxyquinone	—	Plants
Toluene	3-hydroxy-4-methoxy-2, 5-toluquinone	Fumagatin	Cultures
Toluene	3, 6-dihydroxy-4-methoxy-2, 5-toluquinone	Spinulosin	Cultures
Terphenyl	3, 6-dihydroxy-2, 5-diphenyl-1, 4-benzoquinone	Polyphoric acid	Fungus
Terphenyl	2, 5-di-(p-hydroxyphenyl)-3, 6-dihydroxy-1, 4-benzoquinone	Atromentin	Fungus
Naphthalene	2-hydroxy-1, 4-naphthoquinone	Lawsone	Shrub leaves
Naphthalene	2-methyl-3-hydroxy-1, 4-naphthoquinone	Phthiocol	Tubercular bacillae
Naphthalene	1, 3, 4, 5, 6, 7, 8-heptahydroxy-2-ethylnaphthoquinone	Echinochrome	Sea Urchin
Anthracene	1, 2-dihydroxyanthraquinone	Alizarin	Madder root
Anthracene	1, 3-dihydroxyanthraquinone	Purpuroxanthin	Madder
Anthracene	2-hydroxy-3-carboxyanthraquinone	Munjistin	Plant roots
Anthracene	1, 2, 4-trihydroxyanthraquinone	Purpurin	Madder
Anthracene	4, 5, 8-trihydroxy-2-methylanthraquinone	Helminthosporin	Metabolic products
Anthracene	$C_{22}H_{20}O_{13}$ (an anthraquinone)	Carminic acid	Scale insect
Phenanthrene	$C_{20}H_{12}O_9$	Telephoric acid	Fungus
Perylene*	Dihydroxyperylene quinone	Erythroaphin	Fungus
Heterocyclic ring structure			
Oxygen:			
Lactone	$C_{19}H_{14}O_5$ (lactonic carboxylic acid)	Vulpinic acid	Lichens
Lactone	$C_{15}H_{14}O_3$ (β-naphthoquinone)	Dunnione	Mast
Lactone	$C_{18}H_{10}O_5$ (o-hydroxypulvinic anhydride)	Calycin	Lichens
Xanthone	1, 7-dihydroxyxanthone	Euxanthone	Leaves
Xanthone	1, 7-dihydroxy-3-methoxyxanthone	Gentisin	Gentian root
Nitrogen:			
Pyrimidine	$C_6H_6O_2N_4$ (purine type)	Toxoflavin	Bacteria
Pyrimidine	$C_{19}H_{19}O_{11}N_{15}$ (purine type)	Leucopterin	Butterfly
Indole	$C_{16}H_{10}O_2N_2$	Indigo	Indigo plant
Indole	$C_{16}H_8O_2N_2Br_2$	Tyrian purple	Snails
Pyridine	$C_{20}H_{19}O_5N$	Berberine	Plant roots

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* Anderson and Murray (1956).

It is apparent that the biological theory of the origin of petroleum adequately accounts for the presence of many of the minor constituents of petroleum, based on pigments alone. These substances are by no means the major possible biological source of such materials found in bituminous materials. Many of the oxygenated or nitrogenous substances on which pigments are based have not been isolated from petroleum, however, most are formed as degradation products during pyrolysis to produce coal tars. Although the possibilities of chemical changes during coal-tar preparation must be considered, it is apparent that many of the substances exist in related forms in coal. Fieser (1944) lists the chemicals obtained from coal tar. It is interesting that this list includes such unusual compounds as terphenyl, phenanthrene, pyridine, and indole, which also occur in pigments. This circumstantial correlation may be fortuitous but is worthy of further research.

The occurrence and geochemical implications of porphyrins in bituminous materials has been discussed. These pigments are of particular use as tracers of reactions and processes that take place during the formation and diagenesis of petroleum because of their widespread occurrence in plants and animals, the unusual stability of their vanadium and nickel complexes, and their unique spectral characteristics. The carotenoids are of interest in research on recent sediments. However, they generally are not stable enough to withstand geologic aging. The flavones, anthocyanins, and miscellaneous pigments have basic ring structures that are sufficiently stable to justify an expectation that they may be present in bituminous materials, however, their identification is difficult and their relationship to specific source materials is tenuous. Treibs and Steinmetz (1933) observed colored materials, which they termed "graebeite", in extracts of bituminous rocks. These materials were tentatively identified as pigments of an anthraquinone type on inconclusive evidence. However, Blumer (1951), working with fossilized sea lilies, separated hydrocarbon-like materials that were tentatively identified as an alkyl dibenzoperylene and a mixture of several related fossil hydroxyquinone dyes. It was postulated that these dyes were derived from echinochrome (Table 17) or related naphthoquinone dyes.

Pigments of this type often do not have widespread natural occurrence; many occur only in relatively unusual forms of life. For this reason, they do not have general applicability as geochemical tracers. However, this specificity may allow their use in solving some of the specific problems related to the unknown facets of the origin of petroleum.

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CHAPTER 10

GEOCHEMISTRY OF AMINO ACIDS

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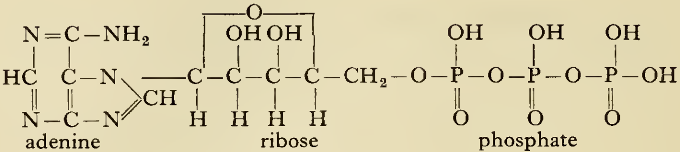
PROTEINS and their amino acids are universal components of all living things. They constitute about half the dry weight of nearly all multicellular animals (Florkin, 1949) and many micro-organisms, and are present to a lesser degree in plants, particularly in the actively growing portions. Proteins play an essential role in the chemical processes of living, acting as catalytic enzymes, and are of paramount importance to the orderly, efficient functioning of life processes. In addition to their occurrence in proteins in soft parts, amino acids are present in bone, hair, and shells, and are components of some "chitinous" materials. Proteins consist mainly of amino acid building blocks which are joined together to make aggregates with molecular weights ranging from a few thousand to many million. About 21 amino acids are commonly employed and the same building blocks appear in a wide variety of creatures. Perhaps a third or even more of the organic materials currently being synthesized over the world's surface are proteins. The quantities of these substances produced each year are enormous and their fate is an important biogeochemical problem.

This chapter will discuss the significance of proteins to present and past life. It will describe briefly some of the present occurrences and chemical properties of the amino acids. Factors controlling destruction or preservation of these substances in nature will be discussed and some of the reported occurrences of amino acids in soils, coals, sediments, rocks, and fossils will be reviewed.

Role of proteins in present and past life—All living forms are veritable chemical factories. In even the simplest bacteria thousands of chemical transformations are necessary to normal life processes. Many of the same chemical steps when carried out in the laboratory require high temperatures incompatible with life. Nature has met the problem of achieving these reactions at low temperatures through the use of protein catalysts. By speeding up certain sequences of reactions they actually regulate many of the living processes. The carbohydrate glucose, for example, can be oxidized chemically in numerous alternative ways, but in the inorganic world comparatively high temperatures are often required if reasonable rates of reaction are to be attained. Through the action of enzymes in living systems, sugar is oxidized rapidly in an orderly sequence of reactions at ordinary temperatures, and the energy is released in a controlled way. One of the important products of carbohydrate metabolism is adenosinetriphosphate (ATP) (Baldwin, 1949). Supplies of this energy-rich compound are stored by all animals and most micro-organisms. Almost every type of energy requirement, including mechanical, electrical, and chemical, is met by ATP. The actual release of the energy is mediated by very efficient protein catalysts.



Adenosinetriphosphate (ATP).

This energy system is particularly important in the functioning of the musculature of most of the phyla. The muscle protein myosin, serving as a catalyst, acts in combination with ATP. In the clam *Mercenaria mercenaria*, as well as in most shelled animals, scars on the shell show the points of muscle attachment, and these are preserved in fossil specimens. The shape of the shell of 25-million-year old specimens is identical to those of today, including the muscle scar. It seems quite likely that the old clams had musculature exactly like that of the modern species and that the highly efficient conventional myosin–ATP system was employed. Similar arguments are applicable to other invertebrates and to vertebrates. In reconstructing extinct forms, paleontologists implicitly assume that the chemical processes involved in muscular activity have not changed to a major degree since early Cambrian times, about 500 million years ago. One may speculate further that other soft parts also contained proteins which were employed in their familiar roles as catalysts.

The principal amino acids—By definition amino acids are chemical compounds which possess amino and acid groups. Tens of thousands of such substances are theoretically possible and many of these have been synthesized.

Only 21 amino acid building blocks commonly occur in proteins of most phyla. In Table 1 are listed the amino acid constituents of some proteins. All the amino acids listed in Table 1 except glycine are optically active and in proteins are principally in the L-form. Important but quantitatively rather inconsequential amounts of the D-forms are found in bacterial peptides including the antibiotics, the polymyxins tyrocidine and gramicidin. About sixty other natural amino acids are known (Meister, 1957) but occur only in nominal amounts.

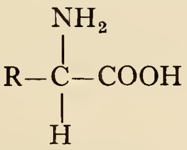
Chemical nature of amino acids—Complete descriptions of the

TABLE 1.

Amino Acid Composition of Some Proteins (calculated as gram of amino acid per 16.0g N)

Amino Acid	Rat, an average	Cod meal	Squid	Lobster shell	Earthworm	Tetrahymena	Yeasts
Arginine	4.5	5.7	12.6	6.6	5.7	5.3	5.4
Histidine	4.0	2.8	2.3	2.5	1.8	2.2	2.5
Lysine	9.0	9.5	10.0	2.9	5.6	5.9	6.6
Tyrosine	2.8	3.2	1.5	6.2	3.7	4.3	3.3
Tryptophan	1.8	0.8	0.3	—	—	0.9	1.1
Phenylalanine	7.5	4.6	2.1	7.1	4.8	5.1	3.0
Cystine	2.8	1.3	—	—	1.0	0.9	1.1
Methionine	2.1	2.9	1.1	0.3	3.0	1.7	1.3
Serine	8.6	4.9	3.2	—	3.7	3.9	4.2
Threonine	7.7	6.1	2.3	6.9	5.0	4.9	4.6
Leucine	10.2	10.2	5.3	7.2	7.8	8.4	6.0
IsoLeucine	3.5	7.6	3.6	7.1	5.5	6.1	4.3
Valine	7.1	6.7	7.7	8.6	6.7	5.1	4.9
Glutamic acid	13.5	20.2	8.2	17.3	11.9	15.0	10.9
Aspartic acid	5.0	12.2	8.1	13.5	8.1	11.9	7.2
Glycine	3.8	5.8	5.9	10.3	4.7	5.1	4.0
Alanine	6.5	5.1	—	12.0	6.6	4.7	5.5
Proline	4.0	6.0	4.3	10.3	—	3.1	4.0
Hydroxyproline	—	—	—	—	—	—	0
References	Müting (1954)	Agren (1951)	Sugimura (1954)	Duchâteau (1954)	Block (1956)	Wu (1952)	Block (1956)

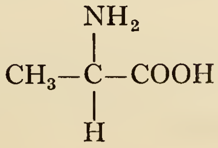
chemical properties and structural formulas of the amino acids may be found in many books, e.g. Meister (1957). However, only a few properties, pertinent to the geochemistry of these substances will be described here. The natural amino acids are white crystalline solids most of which are relatively soluble in water and which are characterized by the structure,



$$R-\underset{\displaystyle H}{\overset{\displaystyle NH_2}{C}}-COOH$$

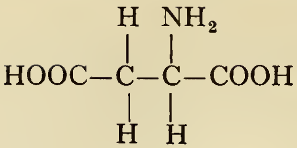
Some typical formulas are:

Alanine



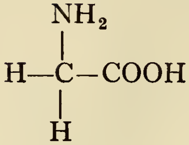
$$CH_3-\underset{\displaystyle H}{\overset{\displaystyle NH_2}{C}}-COOH$$

Aspartic acid



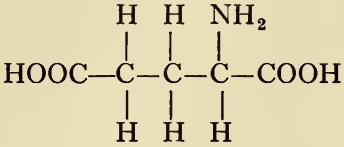
$$\mathrm{HOOC{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{NH_2}{C}}{-}COOH}$$

Glycine



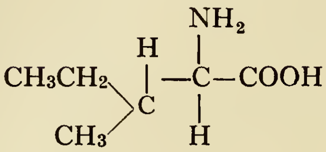
$$\mathrm{H{-}\underset{H}{\overset{NH_2}{C}}{-}COOH}$$

Glutamic acid



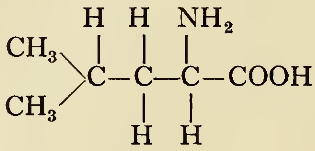
$$\mathrm{HOOC{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{NH_2}{C}}{-}COOH}$$

isoLeucine



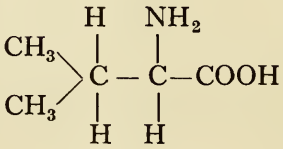
$$\mathrm{\begin{matrix}CH_3CH_2\\ CH_3\end{matrix}\!>\!\overset{H}{C}{-}\underset{H}{\overset{NH_2}{C}}{-}COOH}$$

Leucine



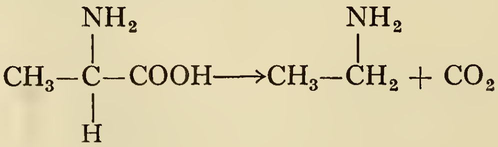
$$\mathrm{\begin{matrix}CH_3\\ CH_3\end{matrix}\!>\!\overset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{NH_2}{C}}{-}COOH}$$

Valine



$$\mathrm{\begin{matrix}CH_3\\ CH_3\end{matrix}\!>\!\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{NH_2}{C}}{-}COOH}$$

Stability of amino acids—Melting points of these substances are: alanine, 297°C; aspartic acid, 270°C; glycine, 290°C; glutamic acid, 249°C; isoleucine, 284°C; leucine, 337°C; and valine, 315°C. These high values are a qualitative indicator of chemical stability, for if decomposition occurred at lower temperatures no such values could be observed. Abelson (1954, 1955) surveyed the thermal stability of amino acids and investigated the thermal behavior of dilute solutions of alanine. Experiments showed that the reaction involved in the degradation of alanine is



$$\mathrm{CH_3{-}\underset{H}{\overset{NH_2}{C}}{-}COOH \longrightarrow CH_3{-}\overset{NH_2}{CH_2} + CO_2}$$

This reaction is first-order and the kinetics should follow the Arrhenius equation

$$k = Ae^{-E/RT}$$

where $dc/dt = - kc$, c is concentration, A is frequency factor $\sim 10^{13}$/sec, E is activation energy, T is absolute temperature, and R is the gas constant.

A series of tests was conducted to determine the time, θ, required for initial concentrations to diminish to $1/e$, or 37 %. Results are shown in Fig. 1. The upper four points on the line were determined using a sensitive C^{14} method (Conway and Libby, 1958). It may be seen that a plot of the log of time, θ, against the reciprocal of absolute temperature gives a straight line. This is in agreement with Arrhenius' equation with a value for the activation energy of $E = 44{,}000$ cals/mol, and a frequency factor $A = \sim 3 \times 10^{13}$ (Vallentyne, 1957). Extrapolation of the linear plot suggests that, near room temperatures, solutions of alanine might persist for a billion years. The sharp dependence of reaction rate on temperature is very important to potential survival of this substance. Most of a sample of alanine would disappear in about 1000 years at 120°C or in a few hours at 250°C. It would be desirable to study this degradation in an environment other than water. Some experiments with calcareous fossils have given results in agreement with the aqueous results, however, incubation of amino acids with other and more reactive matrices, such as organic matter, might lead to very different findings.

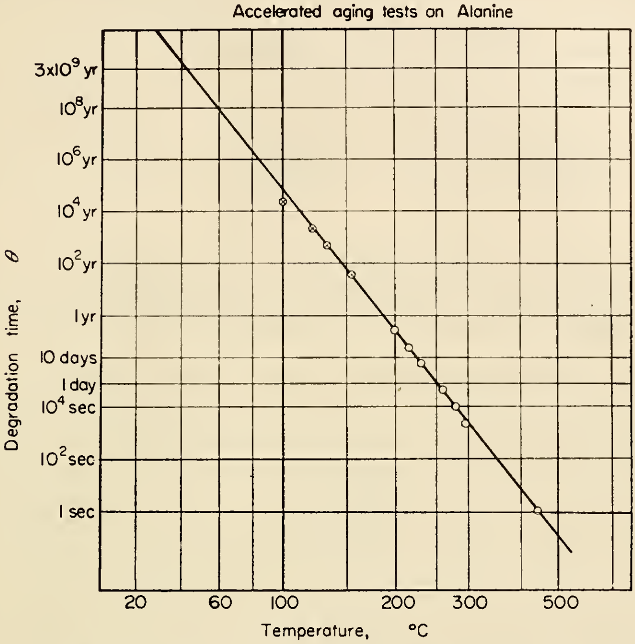
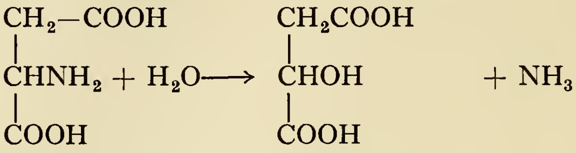


FIG. 1. The thermal degradation of alanine as shown by accelerated tests of aging. Shown is the time required for the decomposition of 63 per cent of the original material. The upper four points were determined by the use of alanine tagged with C^{14} by Dwight Conway at the University of Chicago (from Abelson, 1957).

The thermal stability of aqueous solutions of other amino acids was explored in experiments employing 0.01 molar solutions incubated at 225°–250°C. Alanine, *a*-aminobutyric acid, glutamic acid, glycine, isoleucine, leucine, proline, and valine were found to possess comparable stability. Threonine, lysine, tyrosine, and phenylalanine were moderately stable. Serine was easily destroyed. Tests conducted with aspartic acid are complicated by the fact that this substance partially hydrolyzes into ammonia



$$\begin{array}{l}CH_2\text{—}COOH\\ |\\ CHNH_2\\ |\\ COOH\end{array} + H_2O \longrightarrow \begin{array}{l}CH_2COOH\\ |\\ CHOH\\ |\\ COOH\end{array} + NH_3$$

Aspartic acid Malic acid

and malic acid. Tests on glutamic acid showed that this substance quickly forms a pyrrolidone at high temperatures. Hence, results obtained at high temperatures might or might not be validly extrapolated to other conditions.

Amphoteric properties of amino acids—Those amino acids, such as alanine and glycine, which possess one amino and one carboxyl group are so-called neutral amino acids—at a pH of about 6 they are electrically uncharged in aqueous solution. At higher pH and particularly above pH 9, they behave as anions. At low pH they exist as cations in solution. Indeed, all amino acids exist as anions at sufficiently high pH, and as cations at very low values of pH. These properties are particularly helpful in separation and isolation of the substances. Neutral amino acids are not readily adsorbed on natural materials at ordinary pH. They are soluble in water and are not bound chemically. Aspartic acid and glutamic acid, however, can be adsorbed on $CaCO_3$.

Proteins and amino acids in natural environments—In living organisms virtually all amino acids are linked together in proteins in structures possessing as many as ~100–10,000 building blocks. Only minor amounts of peptides and free amino acids are present. After death, degradative processes are set in motion and autolytic enzymes within the cells of the defunct organisms are freed to initiate hydrolytic and other chemical transformations, including decarboxylations and deaminations. Meister (1957) has reviewed some of the metabolic and enzymatic transformations which can occur. Examples of some of the decarboxylations which he has listed are shown in Table 2.

Even without the intervention of enzymes, proteins tend to disintegrate. In the presence of water peptide bonds linking the amino acids together are hydrolyzed, and even the most insoluble proteins, such as keratins, are converted to more soluble peptides and free amino acids. The processes occurring are exothermic and involve heats of activation of the order of 25,000 calories. The rate of hydrolysis is dependent on temperature, increasing bv a factor of about two for each 10°C rise. The stability of peptide bonds is such that in the presence of moisture in typical geologic environments, hydrolysis requires of the order of 10^4–10^5 years.

Proteins, peptides, and amino acids are affected by many chemicals. Free oxygen combines with all organic chemicals and even at room temperatures rates of reaction are appreciable. Abelson (1957) has estimated that alanine in solution exposed to atmospheric oxygen at ambient temperatures could last only about 10^5 years. Another important reaction involves combination of proteins, peptides, and amino acids with aldehyde groups such as are found in carbohydrates. This reaction proceeds relatively rapidly at low temperatures and might lead to so-called "humic acid"-like substances. Close analysis of actual natural products would probably uncover other examples of chemical reactions with the environmental matrix.

TABLE 2.
Enzymatic Decarboxylation of Amino Acids

Amino acid	Product	Source of enzyme*
L-Arginine	Agmatine	B
L-Aspartic acid	β-Alanine	B
L-Aspartic acid	L-Alanine	B
L-Cysteic acid	Taurine	M
meso-α, ε-Diaminopimelic acid	L-Lysine	B
L-Glutamic acid	γ-Aminobutyric acid	B M P
L-Histidine	Histamine	B M
γ-Hydroxyglutamic acid	α-Hydroxy-γ-aminobutyric acid	B
5-Hydroxy-L-lysine	Hydroxycadaverine	B
L-Lysine	Cadaverine	B
L-Ornithine	Putrescine	B
L-Phenylalanine	Phenylethylamine	B
L-Tyrosine	Tyramine	B

*M = mammalian tissue.
P = plant tissue.
B = bacteria.

Biological agencies are the most important factors in the destruction of protein. Aerobic conditions are particularly favorable for the rapid consumption of proteins which are used as food by most creatures. The major fraction is metabolized by microorganisms which multiply rapidly. For instance, *Escherichia coli* have a generation time of 13 min when conditions, including food supply, are favorable, and can destroy enormous quantities of proteins. Worms and other scavengers which can only exist in at least partly aerobic environments play an important role in destruction of organic matter in soils and in lake and ocean sediments by consuming organic matter, by providing stirring action and by opening paths for better aeration. Given aerobic conditions, moisture, and access, microorganisms completely destroy proteins, except in a few rare cases.

Under anaerobic conditions the chances of organic material being preserved are materially enhanced. No multicellular organism can exist under truly anaerobic conditions. Anaerobic microorganisms are relatively inefficient metabolically and do not multiply rapidly. Soluble proteins which can diffuse into the sphere of action of the organisms are more subject to degradation than, for instance, insoluble keratinous materials. Proteins immobilized in shell or bone are often protected from contact with bacteria.

Isolation, separation and measurement of amino acids—Methods for separation and measurement of amino acids have undergone marked improvement during the past ten years. Isolation of one part per million of these chemicals from soil and fossils is now a simple task thanks to ion exchange chromatography. Separation of mixtures of amino acids is readily achieved by paper chromatography. Detection of as little as 0.1 μg of these substances can be attained through a colorimetric reaction involving ninhydrin.

Isolation of amino acids—Stevenson (1954) has described an effective procedure for extracting amino acids from soil samples. A 50 g sample of finely ground, dry soil from which undecomposed plant residues had been removed by flotation was refluxed for 24 hr with 150 ml of 6N HC1. The mixture was filtered and excess acid volatilized off by evaporation at 50°C *in vacuo*, after which humin was removed by centrifugation. An aliquot of the solution, containing from 20 to 25 mg of α-amino acid nitrogen, was then passed through a 3.2 × 90 cm column of a cation exchange resin, Amberlite IR-120, in the hydrogen form. The column was washed with distilled water until the effluent was neutral to litmus paper, then eluted with 2 l. of 5 per cent aqueous ammonia, followed by 500 ml of distilled water. The eluate was discarded until a positive test was obtained with ninhydrin. Subsequent effluents from the ammonia and second water washings were combined and the ammonia removed by gentle evaporation. This solution contained some aluminum which had been dissolved by the ammonia. Aluminum hydroxide, which was precipitated during neutralization, was filtered off, after which the solution was concentrated to a volume of about 200 ml by evaporation at 50°C *in vacuo*. After making it slightly alkaline with $Ba(OH)_2$, it was evaporated to a paste *in vacuo* to remove all bound ammonia. The residue was taken up in distilled water and barium was removed as the sulfate.

Abelson (unpublished) has employed a similar procedure in the isolation of amino acids from bones, shells, and calcareous fossils. A weighed specimen, 5–50 g, was refluxed with excess 6N HCl for 18 hr following which excess acid was removed by evaporation on a steam bath. The residue was diluted to make a solution about 0.5 M in calcium. Any undissolved residue was removed by centrifugation.

The cation exchange resin used was Dowex-50, 50–100 mesh, 8% cross-linked, and in the hydrogen form. Moist beds of such material occupying a volume of 80 ml in a column 20 cm long and 2.3 cm diam. were employed. Such columns could be loaded with 50 ml of a solution 0.5 M in calcium. After washing with distilled water until the effluent was neutral, the amino acids were eluted with 4 M NH_4OH. On evaporation to dryness on a water bath, a residue of amino acids remained. This residue was usually sufficiently free of inorganic matter so that it could immediately be subjected to paper chromatography.

Chromatographic separation of amino acids—Resin or paper chromatography permits separation and quantitative determination of the amino acid components of complex mixtures. The resin columns are characterized by the following features:

1. Relatively high capacities ~ 3 to >100 mg.
2. Feasibility of quantitative determination.
3. Much effort for an analysis.

Paper chromatography has the following characteristics:

1. Low capacity per chromatogram.
2. High sensitivity (can separate amino acid components in 0.1 mg).
3. Little labor.
4. Large numbers of simultaneous analyses.
5. Ease of qualitative determination.
6. Difficulty of quantitative measurement.

Resin chromatography:

Stein and Moore (1949), Moore and Stein (1951), and Hirs, Moore and Stein (1952, 1954) developed procedures for separation of amino acids on Dowex-50 columns. Their schemes have been used widely and are well regarded by those who have employed them. Hirs, Moore, and Stein (1954) used the anion exchanger, Dowex-1, to obtain an initial removal and resolution of tyrosine, glutamic acid, aspartic acid, and cysteic acid from a hydrolysate of 70 mg of bovine serum albumin, thus easing the problem of resolving the remaining mixture. This latter fraction was split into its components on a 0.9 cm × 150 cm 4% cross-linked Dowex-50 column. The elution schedule and results of the procedure are depicted in Fig. 2. Excess acid can be removed from the eluate aliquots by evaporation, preferably *in vacuo*. The residue is then suitable for use in paper chromatography or for quantitative determination colorimetrically by the ninhydrin method (Troll and Cannan, 1953). Recoveries of amino acids from columns are not entirely quantitative. For instance, only a fraction of original methionine was obtained in the eluate.

A second method (Moore and Stein, 1951) employed 0.9 × 100 cm columns of Dowex-50 resin, 200–400 mesh, 8% cross-linked, and in the Na-form. Amino acids were eluted by a series of buffer solutions with results shown in Fig. 3. Comparison of Figs. 2 and 3 shows that the

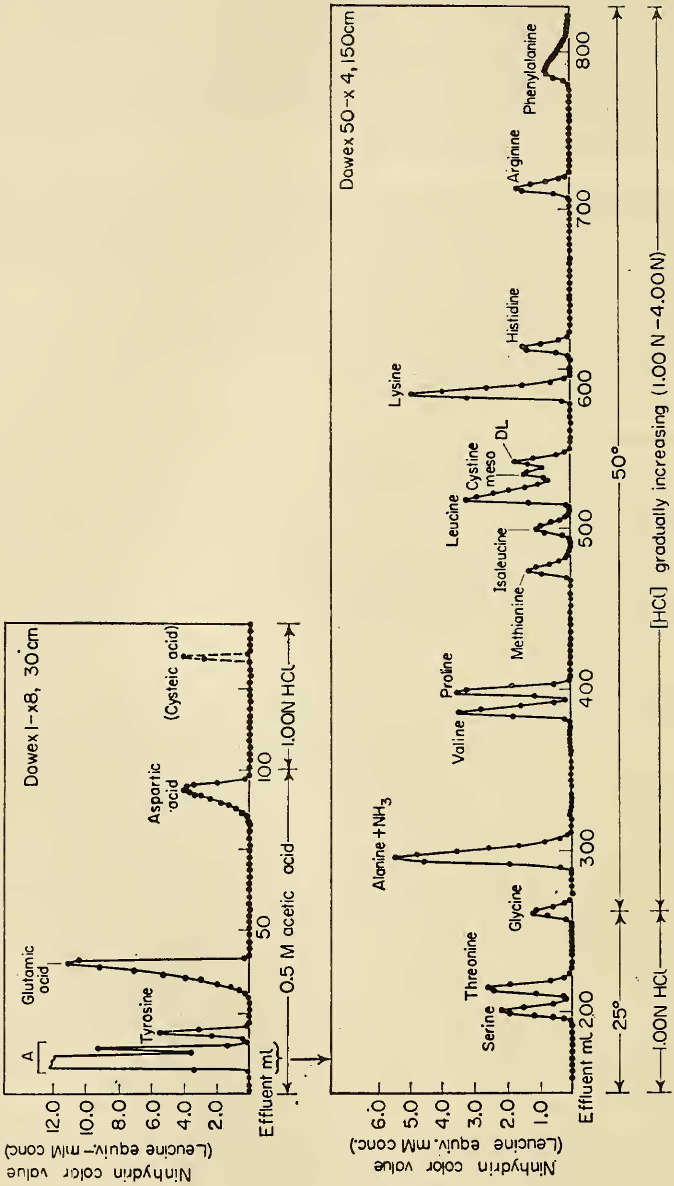


FIG. 2. The elution of amino acids from Dowex –1 X 8 with 0.5 N acetic acid at 25°, and from Dowex –50 X 4 with 1–4 N HCl at 25 and 50° (from Hirs, Moore and Stein, 1954).

order of appearance of amino acids differs in the two cases. Thus, the two methods are supplementary. Eluates from the second scheme are in a form more suitable for ninhydrin colorimetric analysis but the presence of buffer salts interferes with possible paper chromatography of eluates. This difficulty has been overcome by a modification using buffers made of volatile components (Hirs, Moore, and Stein, 1952). When solutions of ammonium acetate or formate are brought to dryness *in vacuo*, the salts sublime, leaving behind the solid amino acids.

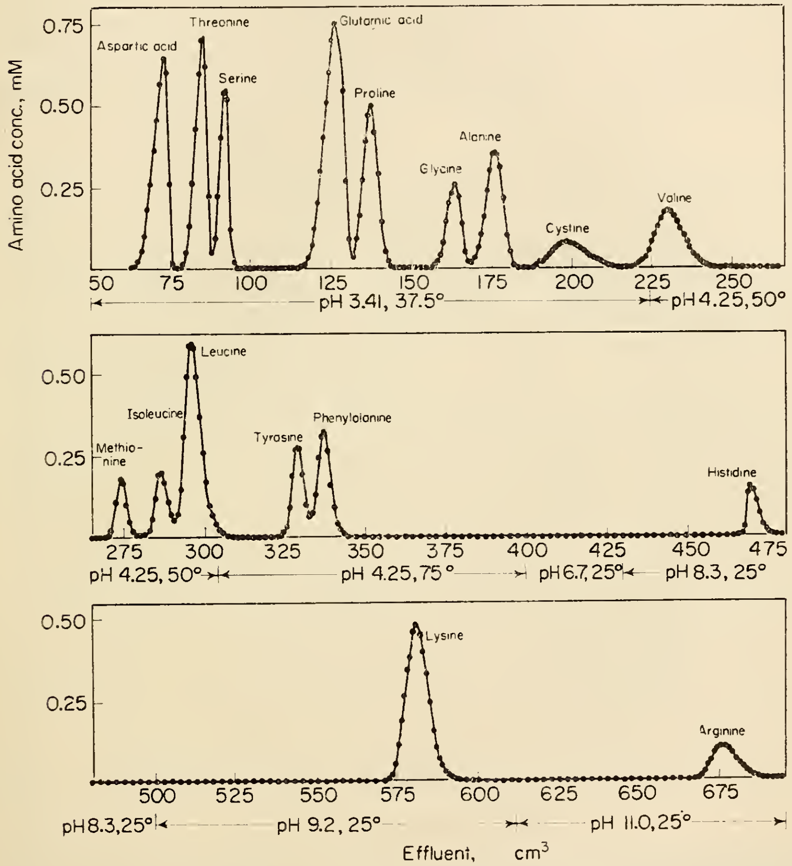


FIG. 3. Separation of amino acids from a synthetic mixture simulating the composition of a protein hydrolysate (from Moore and Stein, 1951).

Paper chromatography:

Paper chromatography is an exceedingly useful method for the separation of amino acids and peptides. A description of the method was published in 1944 by Consden, Gordon, and Martin; since then, thousands of researches have been conducted using the original technique and hundreds of variants on the procedure (Block, Durrum, and Zweig, 1955).

One convenient method is described briefly to illustrate the procedure for two-dimensional separations: A drop of solution containing 0.1 mg of amino acids in a volume of 0.003 ml is placed near the corner of a square sheet (24 cm) of Whatman No. 1 filter paper about 3 cm from two sides. The drop is allowed to dry and the paper is hung in a tank with one edge dipping in a developing solution (70% secondary butanol, 10% formic acid, 20% water, v/V). By capillary action the solvent moves up the paper past the "spot" requiring about 12 hr to travel the length of the paper. At this

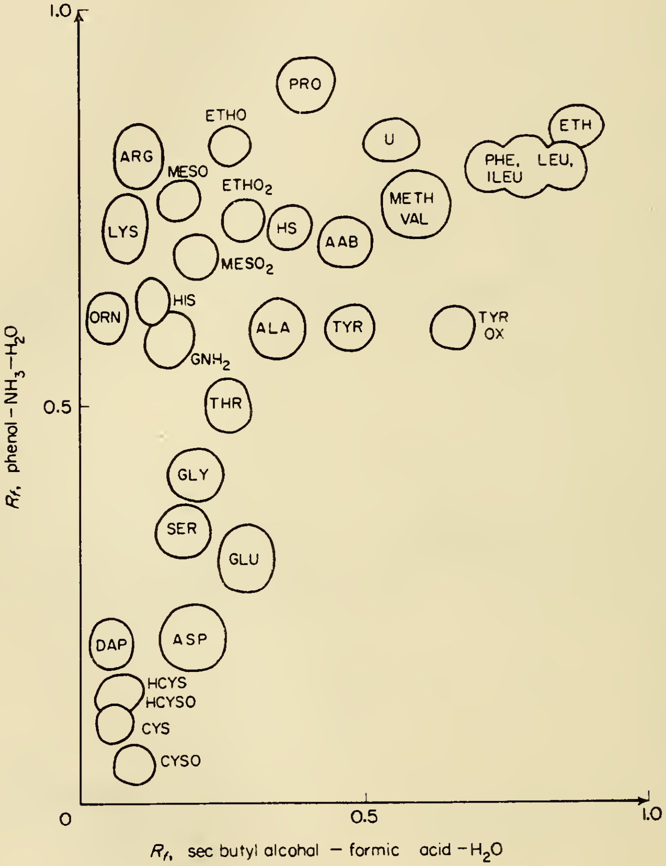


FIG. 4. Map of locations of amino compounds on chromatograms run in sec-butyl alcohol/formic acid/water; phenol/ammonia/water. AAB, α-aminobutyric acid; ALA, alanine; ARG, arginine; ASP, aspartic acid; CYS, cystine; CYSO, cysteic acid; DAP, diaminopimelic acid; ETH, ethionine; ETHO, ethionine sulfoxide; ETHO$_2$, ethionine sulfone; GLU, glutamic acid; GLY, glycine; GNH$_2$, glucosamine; HCYS, homocystine; HCYSO, homocysteic acid; HS, homoserine; HIS, histidine; ILEU, isoleucine; LEU, leucine; LYS, lysine; METH, methionine; MESO, methionine sulfoxide; MESO$_2$, methionine sulfone; ORN, ornithine; PHE, phenylalanine; PRO, proline; SER, serine; THR, threonine; TYR, tyrosine; TYROX, tyrosine (oxidized product); U, urea; VAL, valine (from Roberts, Abelson, Cowie, Bolton, and Britten, 1955).

time the paper is removed from the tank and dried. The chromatogram is turned through 90° and the procedure repeated using a different solvent system containing 80% phenol, 19% water, and 1% concentrated NH_3 solution by weight. The amino acids tend to be carried by the moving liquid with the more hydrophobic substances travelling farthest. At the conclusion of migration in both dimensions the contents of the original "spot" have separated and the various amino acids have travelled to different locations on the paper.

After the paper has been dried, the amino acids are detected by reaction with ninhydrin. This is readily accomplished by dipping the paper in a 0.1% acetone solution of the dye. On warming gently, colored spots appear corresponding in intensity to the amount of amino acid present. A map showing the location of various amino compounds in the two-dimensional chromatogram is shown in Fig. 4.

Amino acids in soils—The amino acid content of soils has been studied by many investigators over the past fifty years. Suzuki (1908) isolated alanine, leucine, valine, proline, and aspartic acid from hydrolysates of "humic acids." Schreiner and Shorey (1910) isolated arginine and histidine from alkaline extracts of soils and detected the presence of lysine. Later discoveries were reviewed extensively by Waksman (1938) and by Kojima (1947) and Bremner (1949).

Development of chromatographic techniques has made feasible new and superior approaches to the problem. Stevenson (1954, 1956a, b) applied these methods to an examination of some Illinois farm soils and obtained quantitative analyses of hydrolysates of the constituent organic nitrogen substances.

The soils studied by Stevenson were taken from the Morrow plots at the University of Illinois; their characteristics have been described by Stauffer *et al.* (1940). The samples were collected from the plow layers of four of the plots, which were an untreated continuous-corn plot (plot 3 NE), the untreated corn-oats rotation plot (plot 4 NE), the treated corn–oats–clover rotation plot (plot 5 SE), and the grass border surrounding the plots. The soils were hydrolysed with 6N HCl and the liberated amino acids were separated by column chromatography. Results are shown in Table 3.

The first 15 amino acids listed are typical constituents of structural proteins. The presence of a,ϵ-diaminopimelic acid is quite significant. This substance is not a constituent of woody plant material but is found only in micro-organisms. Occurrence of this substance in the hydrolysates is indicative that at least part of these amino acids were derived from bacterial proteins. Stevenson (1956a) also identified chondrosamine in soil hydrolysates, and this is further evidence of a microbial contribution to the organic matter of soils. The occurrences of β-alanine and γ-aminobutyric acid in the hydrolysates can be explained as products of the action of bacterial enzymes.

Stevenson (1956a) has suggested that α-amino-n-butyric acid might be derived from reduction during hydrolysis, but the evidence is not entirely convincing. Methionine sulfoxide and cysteic acid are almost certainly products of oxidation of methionine and cystine.

TABLE 3.
Amino Acid Composition of some Morrow Plot Soils

Amino acid	mg/100 g of soil			
	Plot 3 NE	Plot 4 NE	Plot 5 SE	Grass border
Glycine	21.8	26.2	49.8	73.7
Alanine	31.7	38.8	69.5	76.4
Serine	14.0	20.6	43.0	73.4
Threonine	18.2	27.8	42.7	81.0
Valine	21.3	23.5	43.6	62.0
Leucine	19.5	24.0	50.5	63.4
isoLeucine	16.1	19.0	36.8	47.7
Proline	10.3	14.5	30.3	51.7
Phenylalanine	7.4	9.1	16.8	23.6
Tyrosine	8.0	9.5	14.9	23.3
Aspartic acid	26.0	22.4	65.8	66.7
Glutamic acid	20.0	32.8	59.4	94.4
Histidine	5.8	7.2	9.4	6.9
Arginine	6.4	8.5	11.8	17.0
Lysine	44.4	51.0	65.9	70.0
α, ϵ-diaminopimelic acid	2.5	3.0	6.6	9.9
γ-aminobutyric acid	3.5	4.1	8.0	12.0
β-alanine	5.0	6.1	11.0	17.3
Ornithine	8.5	7.1	8.0	8.6
α-amino-*n*-butyric acid	1.0	1.1	2.2	3.5
Methionine	trace	trace	trace	trace
Methionine sulfoxide	11.3	10.4	11.2	22.7
Methionine sulfone	trace	trace	trace	trace
Cystine	trace	trace	trace	trace
Cysteic acid	5.3	6.4	10.3	15.9

The chemical nature of nitrogen in soils is not yet fully known. Stevenson (1954) found that 79% to 81% of the total nitrogen of three soils was acid-soluble, with 29% to 31% of the soluble nitrogen occurring as *a*-amino nitrogen. In addition to occurrence in micro-organisms, this latter fraction might be present in at least several forms: as free amino acids, peptides, and proteins, or as amino acids, peptides, and proteins bound to inorganic soil particles or humic materials.

Most soils contain vast numbers of metabolically active micro-organisms which utilize free amino acids, peptides or proteins. Hence, the presence of any substantial amount of these compounds in soils would be an unlikely event. This point of view has been confirmed by experiments of

Sowden and Parker (1953). Using 1-fluoro-2,3-dinitrobenzene, an agent which reacts with free amino groups, these investigators found no such groups were present in intact soils.

Electrophoretic patterns of the organic colloids extracted from clays have shown that free proteins could not be present in large amounts (Stevenson, Marks, Varner, and Martin, 1952; Stevenson, Van Winkle, and Martin, 1953). Waksman and Iyre (1932) attributed the resistance of soil protein to its combination with lignin but could not cite conclusive evidence. More recently the presence of amino acids in or associated with humic acid preparations has been noted by several investigators including Okuda and Hori (1954, 1956); Bremner (1955); Hayashi (1956); and Blumentals and Swain (1956).

Peats and coals—In view of the occurrence of amino acids in soils, their presence in peats is not surprising. Waksman (1938) and Kirner (1945) reviewed the examples of organic nitrogeneous substances in peats and coals.

Recently, two peats have been studied extensively (Swain, Blumentals, and Millers, 1959). The amino acids from hydrolysates of various zones in Cedar Creek peat from Minnesota and Dismal Swamp peat from Virginia were separated by paper chromatography. Among the amino acids measured were glycine, aspartic acid, glutamic acid, threonine, alanine, valine, and leucine.

A study (Shacklock and Drakeley, 1927) using earlier techniques established the presence of diamino and monoamino acids in peat, lignite, and subbituminous coals. Monoamino, but no diamino, acids were found in bituminous and anthracite coals. The geological age of these latter specimens was not specified but they were presumably Carboniferous. The apparently greater stability of monoamino acids is in accord with thermal stability studies quoted earlier.

Aspartic acid, glutamic acid, and glycine were found (Heijkenskjöld and Möllerberg, 1958) in hydrolysates of a British anthracite coal. The authors did not describe the formation from which the coal was collected, but state that it was about 250 million years old.

Amino acids in sediments—Another environment where amino acids may be found is in sediments and sedimentary rocks. Erdman, Marlett, and Hanson (1956) made a comparative study of the amino acid content of a typical Recent shallow-water marine-deposit and that of a similar sediment laid down approximately 30 million years ago. The Recent sample, collected on the inner continental shelf of the Gulf of Mexico, represents a narrow sedimentary layer at a depth of 120 cm; this is below the zone of major bacterial activity. The age of the sediment is probably not more than a few thousand years. The older sample was a section of a marine shale core cut from the Anahuac Formation in Fort Bend County, Texas, at a depth of 5000 ft. Examination of these materials showed that the modern and ancient marine samples selected for study are quite similar with respect to concentrations of carbonate carbon, organic carbon, and fixed nitrogen. The concentrations of free or combined amino acids were less in the Oligocene sample by a factor of 6; the Recent sediment contained 3.0 μM/g. The nature of the amino acids present was also studied with results shown in Tables 4 and 5. It may be noted that the surviving amino acids were the same ones that were found (Abelson, 1954) in studies on fossils.

TABLE 4.

Comparison of a Recent and an Oligocene Marine Mud

(From Erdman, Marlett, and Hanson, 1956)

Content	Recent	Oligocene
Carbonate carbon, %	0.71	1.49
Organic carbon, %	0.53	0.27
Organic nitrogen, %	0.044	0.032
Amino acids, μM/g	3.0	0.51

TABLE 5.

*Principal Amino Acids in Recent and Oligocene Sediments**

(From Erdman, Marlett, and Hanson, 1956)

Recent	Oligocene
Valine	Alanine
Leucines	Glutamic acid
Alanine	Glycine
Glutamic acid	Proline
Aspartic acid	Leucines
Glycine	Aspartic acid
Proline	
Tyrosine	
Phenylalanine	

*Arranged in order of decreasing abundance.

Amino acids in shells and calcareous tests—Some of the most important occurrences of proteins and amino acids are in fossils. Within calcareous structures such as shells, the substances are protected from bacteria and often are not completely leached away by ground water. If the $CaCO_3$ of a fossil recrystallizes, soluble amino acids are, of course, lost. Many shells consist mainly of aragonite which, on recrystallizing, usually changes to coarsely crystalline calcite. Recrystallization of calcitic fossils can often be detected by noting the appearance of the specimen.

Recent shells and calcareous materials of biological origin have been

TABLE 6.

Amino Acid Content of Various Recent Tropical Calcium Carbonate Shells

Specimen	Description	Mineral composition	Amino acid content*
Porites lichen	Reef-building coral	Aragonite, 10–20% calcite	6.7
Porolithon onkodes	Coralline alga	Calcite with $MgCO_3$ in solid solution	17.6
Chama lazarus	Reef-dwelling clam	Aragonite	16.4
Codakia punctata	Ribbed clam	Aragonite	8.4
Atactodea glabrata	Intertidal clam	Aragonite	42.7
Cymatium muricinum	Thick-shelled snail	Aragonite	20
Tridacna maxima	Man-eating clam	Aragonite	26.6
Cypraea mauritiana	Tropical snail	Aragonite	6.2

The materials were furnished by Preston Cloud, U.S. Geological Survey. The *Porites lichen* and *Porolithon onkodes* were collected at Saipan. The other specimens were collected at Onotoa Atoll in the Gilbert Islands.

* In micromoles per grain, 1 μM/g is approximately equal to 1 part per 10,000.

examined (Abelson, 1954) as a guide to the understanding of occurrences of organic materials in fossils. In Table 6 are shown results of examination of some tropical shells. It will be noted that all specimens listed contained proteins in amounts corresponding to 6 to 40 μM of amino acids per gram. Forty other Recent, arbitrarily chosen, shells were surveyed; all were found to contain protein. The amino acids appearing were those typically found in protein hydrolyzates, with occasional specimens showing additional unidentified components. Block and Weiss (1956) determined the relative amounts of amino acids in proteins associated with shells of marine organisms. Results of their work are shown in Table 7.

Abelson (1955) has reported some observations bearing on the rate of hydrolysis of proteins in shells. The shell of the clam *Mya myarenaria* was employed to check the effect of relatively short exposures to geological environments. Recent specimens of this shell and items dated at 1000 years were compared. Solution of the Recent shell in dilute hydrochloric acid left a residue of filamentous light-colored protein; the 1000-year-old specimen yielded protein which was amber-colored and had only a relatively limited mechanical strength. Tests showed that protein content and amino acid content were identical in the two types of specimen. In another experiment, shells were dissolved in a mixture of dilute hydrochloric acid and trichloroacetic acid. Insoluble protein was removed from the mixture by centrifugation and the clear supernatant solution was examined as to its content of free amino acids, peptides, or soluble protein. A negligible amount was found in each case, showing that the proteins of the 1000-year-old shell had not been broken into fragments of low molecular weight.

For studying older materials, the clam *Mercenaria mercenaria* was a

Table 7.

Amino Acid Composition of some Proteins Associated with Shells (calculated as grams of amino acid per 16.0 g N)

Amino acid	Crab	Lobster	Sea urchin	Oyster	Scallop	Clam
Arginine	4.4	6.6	5.8	2.9	1.6	4.3
Histidine	3.8	2.5	1.1	0.7	0.8	1.8
Lysine	3.8	2.9	4.8	4.3	10.2	3.1
Tyrosine	5.4	6.2	2.0	3.1	0.4	14.7
Tryptophan			1.3	0.5	0	
Phenylalanine	7.3	7.1				2.9
Cystine			0.9	1.0		1.5
Methionine	1.0	0.3	1.0	1.6	1.3	9.6
Serine					14.0	2.7
Threonine	6.9	6.9				2.8
Leucine	9.6	7.2	3.5			2.5
isoLeucine	7.2	7.1				2.8
Valine	11.5	8.6	0.8			3.6
Glutamic acid	19.7	17.3				3.0
Aspartic acid	14.3	13.5				9.6
Glycine	8.7	10.3	6.9	15.7	11.0	28.0
Alanine	8.7	12.0				3.1
Proline	10.8	10.1				3.7
Hydroxyproline						0
Reference	Duchâteau (1954)	Duchâteau (1954)	Roche (1951)	Roche (1951)	Roche (1951)	Block (1956)

convenient object. This edible hard-shell clam, which lives today, is represented by fossil specimens dating back at least 25 million years. Specimens of Pleistocene age were tested which, on geologic evidence, are thought to be in the range of 100,000 to 1 million years old. Comparison of Recent and older specimens revealed that marked changes had occurred in the fossil proteins. The material isolated by the usual protein precipitants was a black, tarry substance which yielded amino acids on hydrolysis. The clear supernatant solution contained peptides and free amino acids. The total amino acid content of the Pleistocene shell was only 18% of that found in Recent shells. When Miocene (25-million-year-old) shells were examined, amino acids were found, but no traces of proteins or peptides could be detected. These results are summarized in Table 8.

Initially most of the protein of the shell is evidently present in water-insoluble layers. For thousands of years only moderate changes occur, which do not affect the solubility of the protein. By the time 1–5% of the peptide bonds are broken (10,000 to 100,000 years), the protein fragments are much more soluble and some can be leached out of the shell. Some of the amino acids or peptides are probably entrapped in the aragonite structure. Ultimately, in the presence of water, these peptide bonds are broken, leaving only free amino acids in the shell. It is of interest to note in Table 8 that the free amino acid content of the shell changed only moderately in the period from 1 million to 25 million years.

TABLE 8.
Amino Acid Content of Mercenaria mercenaria

Age	Amino acid content, μM/g		
	Protein bound	Soluble protein or peptide	Free
Recent	33.0	1.5	<0.35
Pleistocene	2.1	2.25	1.0
Miocene	0	0	0.75

Abelson (1954) studied the amino acid content of a series of fossil materials and in Table 9 are shown results obtained from a series of 25-million-year-old shells. All specimens examined were found to contain amino acids.

TABLE 9.
Amino Acid Content of Fossils from one Locality

Specimen	Description	Mineralogy	Amino acid content, μM/g
Glycymeris parilis	Clam	Aragonite	0.80
Mercenaria mercenaria	Clam	Aragonite	0.75
Melosia staminea	Clam	Aragonite	0.90
Lyropecten madisonius	Scallop	Calcite	1.10
Eucrassatella melina	Bivalve	Aragonite	0.60
Turritella variabilis	Snail	Aragonite	0.40
Ecphora tricostata	Snail	Inner aragonite, outer calcite	1.20
Turritella indenta	Snail	Aragonite	0.50

Fossils collected at Plum Point, Zone 10, Calvert Formation, Maryland, by Wendell Woodring, Kenneth Lohmann, and Philip H. Abelson. Age of shells, about 25 million years.

Amino acids present included alanine, glycine, leucine, valine, glutamic acid, and aspartic acid.

Amino acids in bone—The principal protein in bones is collagen, a fibrous protein found in the mesodermal tissues of animals. Collagen is the main organic component of skin, bone, tendon, and loose connective tissue. Eastoe and Eastoe (1954) examined ox femur using compact bone from which marrow and spongy material had been removed and found

18.64% collagen, 0.24% mucopolysaccharide-protein complex, and 1.02% resistant protein material. Later, Eastoe (1955, 1957) examined the amino acids in collagen derived from a number of vertebrates and, in addition, assayed the amino acids in a number of gelatins derived from collagens. Gelatin is a product which can be prepared as a breakdown product of collagen by extracting these tissues with hot water; the two proteins are practically identical in composition. Some of Eastoe's results are shown in Table 10.

The similarity in values obtained is indeed striking and indicates that probably all vertebrates synthesize collagens which are remarkably alike. It seems permissible to speculate that even extinct vertebrate forms employed collagens of similar compositions.

Amino acids in fossil human bones have been studied by Ezra and Cook (1957) who investigated a series of 20 fossil human and three fossil animal bones representing a time span from recent to archaeologically very old. In bones exposed to burial for short periods most of the amino acids found in fresh bone are present in their normal amounts. In bones older than 5000 years, the amino acids are no longer all present. Aspartic acid, glycine, and glutamic acid were detected in some of the oldest specimens and only aspartic acid was found in a very ancient specimen. Other very old specimens contained no detectable amino acids.

In earlier work Heizer and Cook (1952) and Cook and Heizer (1953a, b) attempted to use the rate of disappearance of organic matter from bone as an auxiliary dating scheme calibrated by C^{14} methods. This effort did not succeed very well. Perhaps the difficulty lies in the fact that degradation of proteins is a function of other variables besides time. Variations in moisture, temperature, pH of the environment, and oxygen tension could greatly affect the hydrolysis and ultimate leaching of proteins and their components. Examples of very favorable environments for preservation are the tar pits at La Brea in Los Angeles. There an asphalt matrix provided an essentially sterile, anaerobic environment in which the concentration of water was very low. Fossils were preserved for 15,000 years (Flint, personal communication), and total amino acid content of several specimens of bone was 10–12%. Studies of the peptide linkage showed that there were virtually no free amino acids and that the amino acids remained linked together. In such an environment proteins and peptides could be preserved for very long times. Abelson (1954) has examined a number of much older fossil bones.

In Table 11, results from a wide variety of fossils may be noted. Specimens were chosen from formations likely to have had a mild thermal history. These results show no trend with time, which is not too surprising, since different burial histories were involved. Actually, the oldest fossil in this group was richest in amino acids. By means of radioactive tracers, amino acids from fossils have been shown to be identical with present-day compounds. The dinosaur bones and the Devonian fish plate yielded only amino acids commonly employed by modern animals.

TABLE 10.
Amino Acid Composition of Vertebrate Collagens and Gelatins
(Eastoe, 1955, 1957)

	Sturgeon swim-bladder collagen	Cod-bone gelatin	Shark-skin gelatin	Lung-fish skin collagen	Whale-skin gelatin	Ox-bone collagen	Human bone collagen	Human tendon acid extract
Alanine	11.6	10.4	11.2	11.7	10.8	10.5	10.9	10.3
Glycine	27.7	28.2	26.5	24.0	26.7	25.3	25.8	25.4
Valine	2.31	2.32	2.71	2.56	2.64	2.65	2.97	3.10
Leucine	2.55	3.26	3.32	3.37	3.56	3.93	3.60	3.57
isoLeucine	1.65	1.64	2.71	1.64	1.57	1.73	1.88	1.53
Proline	12.8	12.4	13.9	14.8	16.2	14.7	15.3	15.2
Phenylalanine	2.53	2.04	2.43	2.60	2.32	2.88	2.49	2.46
Tyrosine	0.46	0.63	0.26	0.19	0.72	0.56	0.86	0.69
Serine	5.8	7.9	5.0	4.71	4.71	4.24	4.06	4.05
Threonine	3.79	3.22	3.24	3.18	3.12	2.52	2.35	2.30
Methionine	1.43	2.26	1.59	0.59	0.79	0.80	0.84	0.90
Arginine	10.0	9.1	9.3	9.1	9.5	9.2	8.8	8.9
Histidine	0.83	1.24	1.26	0.80	0.96	0.96	0.96	0.87
Lysine	3.46	3.66	3.76	3.63	4.14	4.11	4.40	3.29
Aspartic acid	6.9	7.5	6.0	6.6	6.7	7.1	6.7	6.7
Glutamic acid	11.4	11.4	10.3	11.9	11.2	11.9	11.4	11.1
Hydroxyproline	11.8	8.3	10.9	9.8	12.8	14.1	14.1	12.6
Hydroxylysine	1.90	1.42	0.82	0.88	1.02	1.12	0.62	1.50
Total	118.9	116.9	115.2	112.05	119.5	118.3	118.0	114.5

Values are given as grams of amino acid per 100 g of dry ash-free protein.

TABLE 11.
Amino Acid Content of Various Fossils

Name	Approximate age (years)	Formation	Amino acid content (μM/g)	Principal constituents
Plesippus (prehistoric horse)	Late Pliocene 5×10^6	Hagerman Lake Beds, Idaho	0.6	Ala, gly
Plesippus (prehistoric horse, tooth)	Late Pliocene 5×10^6	Hagerman Lake Beds, Idaho	1.5	Gly, ala, leu, val, glu
Mesohippus (prehistoric horse, tooth)	Oligocene 40×10^6	White River, Nebraska	0.31	Ala, gly
Mosasaurus (dinosaur)	Cretaceous 100×10^6	Pierre Shale, South Dakota	1.8	Ala, gly, glu, leu, val
Anatosaurus (dinosaur)	Cretaceous 100×10^6	Lance, Lance Creek, Wyoming	2.8	Ala, gly, glu, leu, val, asp
Stegosaurus (dinosaur)	Jurassic 150×10^6	Morrison, Como Bluff, Wyoming	0.26	Ala, gly, glu
Dinichthys (fish)	Devonian 360×10^6	Ohio Black Shale	3.0	Gly, ala, glu leu, val, asp

Specimens were furnished from the U.S. National Museum by C. Lewis Gazin and David H. Dunkel.
Ala: alanine; asp: aspartic acid; glu: glutamic acid; gly: glycine; leu: leucine; val: valine.

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CHAPTER 11

GEOCHEMISTRY OF CARBOHYDRATES *

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Introduction

IT is the purpose of this chapter to review the work that has been done on the isolation of carbohydrates and related compounds from geologic material.

Carbohydrates deserve a special place in any treatment of organic geochemistry because of their high content in plant tissues relative to proteins and lipids. Also, a carbohydrate (cellulose) was one of the first organic compounds of unquestioned biological origin to be isolated from fossil material (Gothan, 1922). Several significant contributions have been made to the geochemical study of carbohydrates over the past thirty-five years, with the result that the carbohydrates now stand among the better known classes of organic compounds from a geochemical point of view. That is not to say that the information is relatively complete, for nothing could be farther from the truth. The stage in development is comparable to an artist's preliminary sketch of a painting: only a few crude strokes here and there, which depict the general form of the picture to come.

Early work on the geochemistry of the carbohydrates was hindered by the lack of adequate methods of purification and identification, particularly when dealing with small amounts of material. The surge in the development of chromatographic and electrophoretic methods of separation within the past ten years has partly alleviated these difficulties, but even at the present time new carbohydrates are coming to light, and the detailed study of large carbohydrate molecules is still in its infancy.

The topics to be discussed in this chapter are: (a) the structure and classification of carbohydrates; (b) some methods used in the study of carbohydrates; (c) carbohydrates found in living organisms; and (d) carbohydrates found in geologic materials.

Primary attention has been given only to those investigations in which serious attempts have been made to determine molecular structure; the viewpoint of this chapter is, therefore, qualitative rather than quantitative.

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* The bulk of this chapter was written when the author was in the Department of Biology, Queen's University, Kingston, Ontario, Canada. Manuscript submitted in 1958 and revised in 1962.

Structure and Classification of the Carbohydrates

Carbohydrates are defined as ketonic and aldehydic derivatives of polyhydric alcohols. However, it is also usual to include some naturally occurring carbohydrate derivatives in discussions of carbohydrate chemistry. The simplest molecules of the carbohydrate type are the sugars or *monosaccharides* (suffix = -ose), which vary from four to seven carbon atoms in chain length. Thus there are tetroses, pentoses, hexoses and heptoses. Both ketonic and aldehydic derivatives exist for each of these classes (e.g. ketohexoses and aldohexoses). The open-chain formulas of the four-five- and six-carbon aldoses related to D-glycerose are shown in Fig. 1.

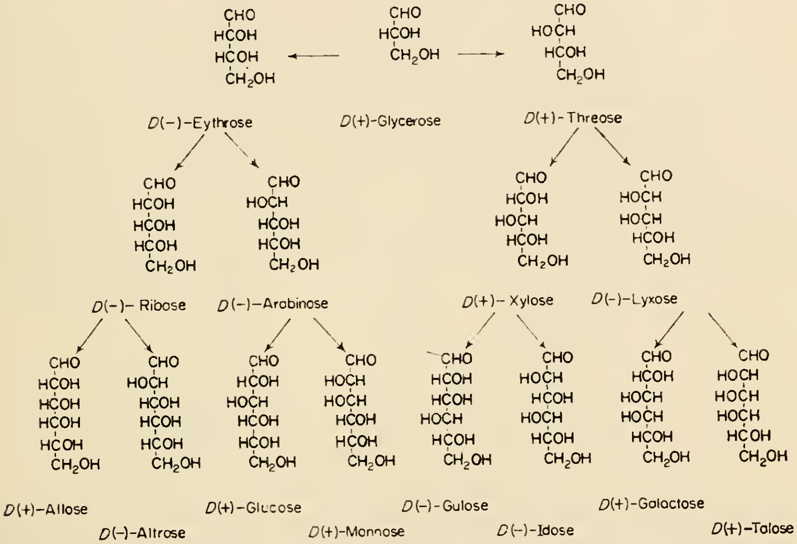
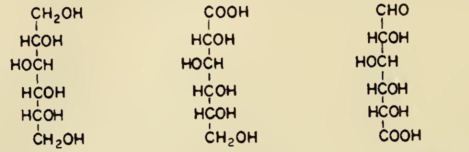


FIG. 1. Open-chain formulas of the tetroses, pentoses and hexoses related to D-glycerose.

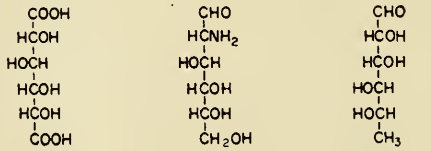
When two or more monosaccharides are united by a dehydration process, a disaccharide, trisaccharide, tetrasaccharide. . . polysaccharide results. The lower members of the series (from two to six monosaccharide units) are referred to as oligosaccharides. It is important to note that the chemical bond uniting two sugars *always involves at least one potentially reducing group* (i.e. aldehyde or ketone group). Sometimes two reducing groups may be involved, as in the disaccharides sucrose and trehalose, which are, therefore, non-reducing sugars. The bond uniting two monosaccharides is called a *glycosidic bond*. The hydroxyl groups of a given sugar that are not involved in glycosidic bonds (e.g. in polysaccharides), may participate in the formation of esters, ethers, phosphates, or sulfates, or may be replaced by amino groups. The open-chain formulas and terminology of some common sugar derivatives are shown in Fig. 2.

Sugars may occur in combination with various other organic compounds as *glycosides.* In the glycosides the noncarbohydrate part of the molecule is referred to as the aglycone. It is important to note that pentoses are constituents of the nucleic acids and that they also occur in some co-enzymes.

The valence bonds uniting paraffinic carbon atoms are separated in space by the tetrahedral angle of 109° 28′. One may think of these bonds as resembling the four arms (three basal, one vertical) of a music stand, so adjusted as to have equal angles between any two arms. The structural formulas in Figs. 1 and 2, although useful for symbolic representation, do not depict the three-dimensional form of sugar molecules. It can be shown that two different space isomers can be formed when four different groups are attached to a carbon atom through single covalent bonds. These two forms are mirror images. A carbon atom with four different groups attached to it is termed an *asymmetric carbon atom.* For each asymmetric carbon atom in a molecule, two stereoisomers (space-isomers) are possible. In a molecule with *n* asymmetric carbon atoms there are 2^n theoretically possible stereoisomers. In the aldohexoses (as depicted in Fig. 1) four asymmetric carbon atoms are evident, and 2^4 or 16 stereoisomers can be formed, eight of which are shown in Fig. 1. The other eight are the corresponding L-aldohexoses (mirror images of the D-aldohexoses shown). Of the sixteen chemically distinct aldohexoses, only four occur biologically, namely, D-glucose, D-mannose, D-galactose, and L-galactose. In the 2-ketohexose series there are only three asymmetric carbon atoms per molecule, and only eight stereoisomers (i.e. 2-ketohexoses) can exist.



D-Sorbitol *D*-Gluconic acid *D*-Glucuronic acid

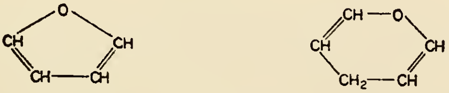


D-Glucaric acid *D*-Glucosamine *L*-Rhamnose

FIG. 2. Open-chain formulas of some common sugar derivatives.

By convention, the numbering of carbon atoms in a sugar molecule is started at the reducing end. If the asymmetric carbon atom furthest from the reducing end has a hydroxyl group on the right when the molecule is viewed in a defined way with the reducing end uppermost (see Fig. 1), the sugar is said to be of the D-configuration. Its *enantiomorph* (mirror image), with the hydroxyl group on the left of the penultimate carbon, is the same sugar in the L-configuration. Enantiomorphs (e.g. D-glucose and L-glucose) have the same chemical properties but differ markedly in biological properties because enzymes can distinguish between them. Non-enantiomorphic stereoisomers (e.g. D-glucose, D-mannose, L-galactose, etc.) are distinct both in their biological and chemical properties.

Solutions of single enantiomorphs are optically active, that is, they rotate the plane of polarization of a beam of plane-polarized light. The rotation exhibited by a solution containing 1g of substance per milliliter of solution in a tube 10 cm long is called the *specific rotation*, symbolized as $[\alpha]_D^t$, when the D line of sodium is used as the light source and the temperature of the solution is *t*. Rotation is said to be (+) if light is rotated to the right of the observer, and (—) if to the left. The degree of rotation depends on the structure of the compound, the wave length of the light, the number of molecules in the light path, and the temperature of the solution. The sign of rotation bears no simple relation to the D- and L-configurations of different sugars. The D- and L-notations only refer to the spatial relationship between the hydrogen and hydroxyl groups on the penultimate carbon atom and not to the dextro- or levorotation of a beam of plane polarized light.



Furan Pyran

FIG. 3. Structural formulas of pyran and furan.

D-Glucose in solution does not behave as a single chemical substance—when freshly dissolved in water, the specific rotation is +112°, but this value falls on standing (the process is catalyzed by a trace of alkali) to + 52.7°. This change in specific rotation with time, eventually reaching an equilibrium value, is called *mutarotation* and is characteristic of all mono- and disaccharides that possess a potentially free aldehyde or ketone group. The suggested explanation of this seemingly odd phenomenon requires that the sugar molecule must exist in two heterocyclic ring forms. While there is good evidence to show that aldoses do possess an aldehyde group, as the formulas in Fig. 1 indicate, the failure to react with certain aldehyde reagents under normal conditions points to a partial masking of the aldehyde group. This masking is brought about by the formation of five- and six-membered heterocyclic rings that involve the reducing group. These ring forms are termed furanose and pyranose rings, respectively, from analogy with the structures of furan and pyran as shown in Fig. 3.

In all monosaccharides the pyranose form is the dominant and more stable structure, however, in oligo- and polysaccharides some sugars are present in the furanose form. The cyclic forms of D-galactose that are in equilibrium with the aldehydo-form are shown in Fig. 4. Equilibrium greatly favors the pyranose forms.

In order to show the spatial relationships of atoms in ring structures, the ring is conventionally depicted with the lower valence bonds thickened so as to make it appear that the plane of the ring is at right angles to that of the paper with the thickened edge foremost. The hydrogen and hydroxyl groups project above and below the plane of the ring, however, the hydrogen atoms are usually omitted for brevity. The cyclic forms of some common monosaccharides and related compounds are shown in Fig. 5. Each of the free bonds opposite the hydroxyl groups has a hydrogen attached to it.

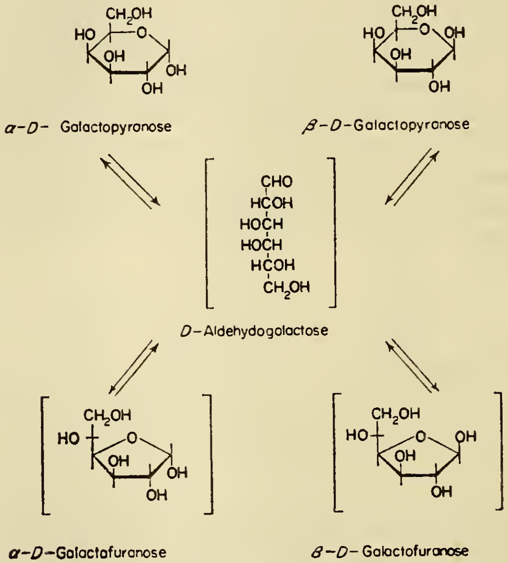


FIG. 4. The molecular forms of D-galactose in aqueous solution. The pyranose forms predominate.

It will be noted that a new asymmetric carbon atom (C^1) is formed by introducing a ring into the sugar molecule. A given sugar in the ring form, such as D-galactopyranose, can exist in two different stereoisomeric states: α-D-galactopyranose in which the hydroxyl on C^1 lies below the plane of the ring as it is ordinarily viewed, and β-D-galactopyranose in which the reverse is true. The α- and β-isomers on C^1 are termed *anomers*, and C^1 is referred to as the anomeric carbon atom. The spatial relations about the anomeric carbon atom differ from those of other asymmetric carbon atoms only in one important respect, their ease of interconversion, especially in the presence of traces of alkali or acid. This conversion proceeds through the intermediate aldehydo-form, as shown in Fig. 4.

The phenomenon of mutrarotation, explained on this basis, represents an approach to equilibrium concentrations of two anomers from an initially high concentration of one through intermediate formation of the aldehydo-form. In the case of D-glucose, the initial specific rotation of + 112° is that of α-D-glucopyranose. β-D-Glucopyranose, with $[\alpha]_D^{20} = +18.7°$, is formed on standing. At equilibrium, a mixture of the two anomers is present with a resultant $[\alpha]_D^{20}$ of + 52.7°. The relative amounts of the two anomers present at equilibrium vary slightly from one sugar to another, but in all cases the pyranose anomers predominate over other conceivable molecular forms.

The spatial relationships about the anomeric carbon atom cannot be interchanged when the C^1 hydroxyl is involved in a glycosidic bond inasmuch as the aldehydo-intermediate cannot be formed without rupturing the glycosidic bond. As a result, the groups about the anomeric carbon atom become fixed in space. The nature of the glycosidic bond (whether α or β) becomes important in determining the form of oligo- and polysaccharides. Both cellulose and amylose, for example, are glucans (polyglucoses) united by 1:4 bonds. In cellulose the 1:4 linkage is β and the cellulose molecule is a linear structure; in amylose the 1:4 linkage is α giving the molecule a coiled form. Hydrolytic enzymes attack glycosidic bonds differentially depending on the configuration of the anomeric link. The enzyme *cellulase* accelerates the hydrolytic cleavage of cellulose, but not of amylose; and the opposite is true for the enzyme *amylase.*

Two main groups of polysaccharides can be delineated: *homopolysaccharides,* (homoglycans), which are polymers of a single monsaccharide or related substance, and *heteropolysaccharides* (heteroglycans), which are composed of more than one kind of monosaccharide. Homopolysaccharides may be further specified by the nature of the unit. The ending *-ose* for sugars is replaced by *-an* to designate a homopolysaccharide (e.g. glucans are polyglucoses; mannans, polymannoses; and galacturonans, polygalacturonic acids). Data from the analysis of polysaccharide mixtures are often expressed in terms of mannans, pentosans (the term pentans has not yet come into common use), etc., without implying anything about the polysaccharide structures in which these units existed. The terms pentosan, araban, polyuronide, etc., may therefore simply mean polysaccharides containing these units as part of their structures, or, polysaccharides completely composed of these units. The term *hemicellulose* is an ill-defined term used to designate polysaccharides other than cellulose, starch, and glycogen, but the name appears to be dropping out of use as the knowledge of polysaccharides develops.

Methods of Isolation and Identification

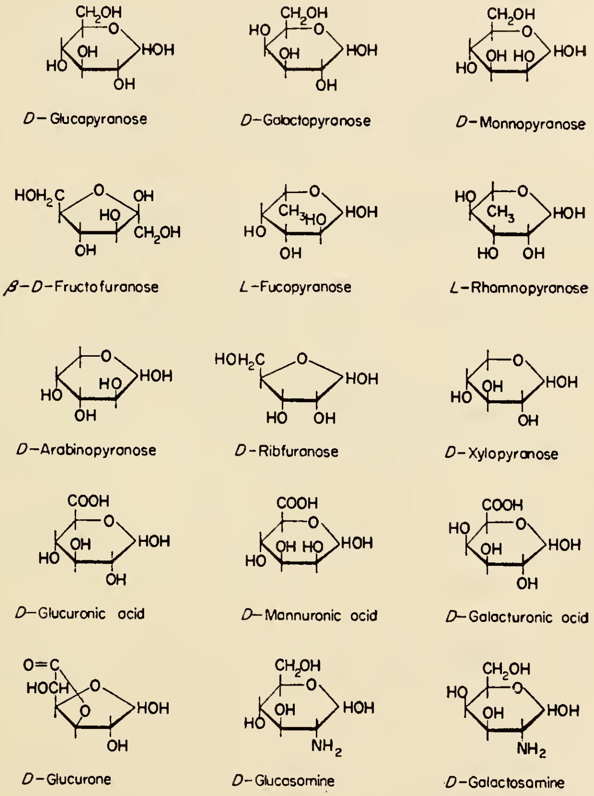
Only a resumé of the more significant methods commonly used in the study of carbohydrates will be presented. This discussion is intended to make the more chemical sections comprehensible to those not familiar with carbohydrate chemistry. Several authoritative texts listed in the bibliography are available to the interested reader.

"Proximate" methods of analysis for carbohydrates have been used extensively in the past, particularly by soil and sediment chemists. Proximate analysis refers to the quantitative determination of general classes of compounds in crude mixtures; the analytical scheme of Waksman and Stevens (1928) has been most extensively used. A dried sample (of plant, soil or sediment) is extracted first with ether, then successively with cold water, hot water, and ethanol. Reducing substances are determined in the aqueous and ethanolic extracts after the insoluble residue has been hydrolysed with 2% HCl. The reducing substances liberated by the acid hydrolysis are calculated in terms of anhydro-glucose units and expressed as hemicelluloses. Cellulose is not readily hydrolyzed by weak acids unless pretreated with more concentrated acid (thus swelling the cellulose fiber). Cellulose is accordingly determined by allowing the insoluble residue from the 2% HCl hydrolysate to stand for several hours in cold 72–80% H_2SO_4, followed by dilution with water and hydrolysis in boiling, dilute acid. The reducing substances liberated by the second hydrolysis are calculated in terms of anhydro-glucose equivalents and expressed as cellulose. It is important to bear in mind that it is really the ease of attack by dilute and concentrated acids that is being measured, rather than the exact nature of the carbohydrates present.

Pentosans may be measured separately by determining the furfuraldehyde produced on distillation of a sample with 12% HCl. Under comparable conditions methylpentosans yield methylfurfuraldehyde, which can be measured separately. Polyuronides may be determined by measuring the carbon dioxide (from the decarboxylation of uronic acids) that is formed on heating a soil sample with 12% HCl; however, the values may be high inasmuch as some other organic compounds will yield carbon dioxide under the same conditions. Lynch, Hearns and Cotnoir (1957) recently developed a more satisfactory method based on the colorimetric reaction of uronic acids with carbazole for determination of polyuronides in the fulvic acid fraction of soil organic matter. Total hexosamines in hydrolysates can be determined using ion-exchange columns and a colorimetric reaction produced with Ehrlich's reagent (Stevenson, 1957b).

Although a reproducible estimate of the total quantity of a certain class of compound, such as hemicelluloses, cellulose, etc., is obtained using proximate methods, there is always doubt as to what actually was measured. On the other hand, quantitative results are seldom obtained when isolating specific compounds from complex mixtures because of losses during the purification procedure. As a result, the two approaches (proximate analysis and analysis for specific compounds) are generally supplementary. The former widespread use of proximate methods in the study of soil organic matter appears to be giving way to more detailed studies of specific substances.

A variety of chromatographic and electrophoretic methods are available for the separation and identification of mono- and oligosaccharides. Figure 6 shows a tracing from a one-dimensional paper chromatogram in which sugars in a standard mixture and those in an ethanolic extract of a lake sediment were separated. The positions of the sugars on the developed chromatogram were revealed by specific spray reagents. Similar resolutions of a sugar mixture can be achieved by paper electrophoresis or column chromatography. Inorganic salts usually interfere with the separation process, however, these may be removed by prior treatment with appropriate ion-exchange resins.



D-Glucopyranose

D-Galactopyranose

D-Mannopyranose

β-*D*-Fructofuranose

L-Fucopyranose

L-Rhamnopyranose

D-Arabinopyranose

D-Ribfuranose

D-Xylopyranose

D-Glucuronic acid

D-Mannuronic acid

D-Galacturonic acid

D-Glucurone

D-Glucosamine

D-Galactosamine

FIG. 5. Structural formulas (in the ring configuration) of monosaccharides and some related derivatives. The furanose forms shown depict the state of the monosaccharide in a polymer.

It is always desirable to chromatograph unknowns in several solvent systems, both alone and mixed with their suspected counterparts in order to be sure of correct identifications. Failure to separate two or more compounds under different chromatographic conditions does not imply identity, merely inseparability under the conditions used. Unequivocal identification requires that the worker isolate the carbohydrate as a crystalline substance or crystalline derivative on which further tests such as melting point, specific rotation, formation of derivatives, infrared absorption, etc., can be performed.

Contact with alkali must be avoided when working with free sugars because it brings about oxidative degradation as well as keto-enolization on C^2 (the "epimeric" carbon atom). To illustrate the latter process, D-glucose in an alkaline medium undergoes a keto–enol shift between C^1 and C^2, resulting in the formation, in part, of D-mannose and D-fructose in a solution that originally contained only D-glucose. This process is called *epimerization.* It does not occur in the internal units of polysaccharides, but may occur in all sugars that possess reducing groups.

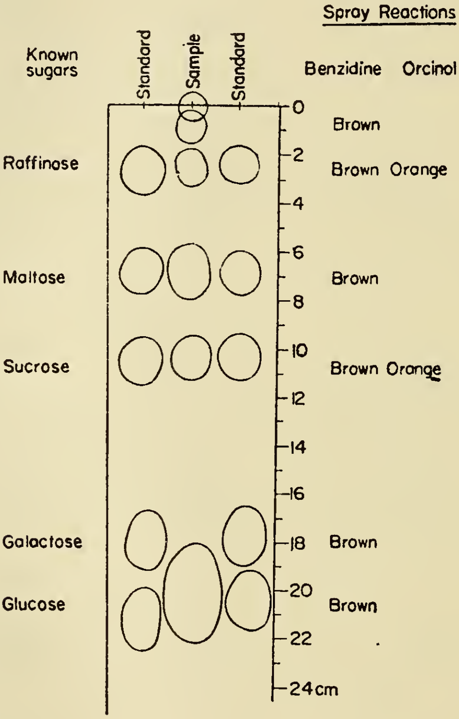


FIG. 6. A tracing of the upper part of a paper chromatogram in which standard sugars and sugars in an ethanol extract of lake mud were separated. The solvent was butanol–ethanol–H_2O (45:5:50) with development for 72 hr. The "sample" spot in the raffinose region did not react with the orcinol spray reagent. (From Whittaker and Vallentyne, 1957.)

Various methods are used in the isolation and purification of polysaccharides. Low molecular weight polysaccharides may be extracted with water and are often precipitated by the addition of organic solvents that are miscible with water, such as ethanol or acetone. Water-insoluble polysaccharides may be extractable with dilute alkali. In the study of wood carbohydrates, the wood is usually first extracted with an organic solvent to remove resins, waxes, or other water-insoluble encrusting material, then repeatedly chlorinated to remove lignins. This treatment leaves a residue of "holocellulose" which is generally taken to represent all the wood polysaccharides. Extraction of the holocellulose with 17.5% NaOH leaves a residue of high molecular weight cellulose called α-cellulose; the extract contains the wood hemicelluloses plus some low molecular weight celluloses (β- and γ-celluloses).

Once a polysaccharide has been isolated in crude form it is subjected to further purification procedures, either as such, or as a prepared derivative. Dialysis, repeated precipitation, partition between immiscible solvents, electrophoresis, and ultracentrifugation may be employed.

In elucidating the structure of a polysaccharide it is not just enough to know the components liberated by hydrolysis; additional information on the manner in which the components were linked together should be obtained by partial hydrolysis of the material followed by isolation of di- and trisaccharides. The nature of the glycosidic linkages is known for most of the lower oligosaccharides. Methylation of the free hydroxyl groups in a polysaccharide may also be carried out to form methyl ethers. The *O*-methylated sugars are isolated after hydrolysis of the *O*-methylated polysaccharide in methanolic HCl. Tetra-*O*-methylhexoses are the most highly methylated monosaccharides found. Tetra-*O*-methylhexoses are formed from terminal units in a polysaccharide chain; tri-*O*-methylhexoses, from internal units; and di-*O*-methylhexoses, from internal units with attached side chains. For example, methylation of cellulose (see Fig. 7 for the structure of cellulose) yields only 2, 3, 6-tri-*O*-methyl-D-glucopyranose on hydrolysis, indicating that the glucose units are linked 1:4 (the C^5 hydroxyl is involved in the pyranose ring), and that the polymer must be long and unbranched (absence of tetra-*O*-methyl-D-glucopyranose).

The anomeric structure of the glycosidic linkage can be inferred from the isolation of disaccharides of known constitution, attack by specific enzymes, or specific rotation values for the intact polysaccharide.

Molecular weights of polysaccharides may attain values of several million. The molecular weight can be estimated by several methods: end-group analysis, osmotic pressure, specific viscosity, or ultracentrifugation. Agreement among methods is often poor and interpretation difficult.

Several authoritative and comprehensive treatments on the carbohydrates are available. Percival (1950) gives a well-balanced treatment that assumes little prior knowledge of the subject by the reader. Whistler and Smart (1953) and Pigman (1957) offer more detailed texts that serve as excellent reference works. Biological and biochemical information about plant polysaccharides has been summarized by Bonner (1950) and by Fogg (1953). Hough and Jones (1956) have summarized information on the biosynthesis of monosaccharides. Also available are: a valuable compendium on cellulose edited by Ott, Spurlin and Grafflin (1943), a text on pectic substances by Kertesz (1951), and a volume on the biochemistry of the aminosugars by Kent and Whitehouse (1955).

The annual series "Advances in Carbohydrate Chemistry" should be consulted for up-to-date review articles in various aspects of the subject matter. In addition, a new five-volume work is currently in preparation by Academic Press on "Methods in Carbohydrate Chemistry".

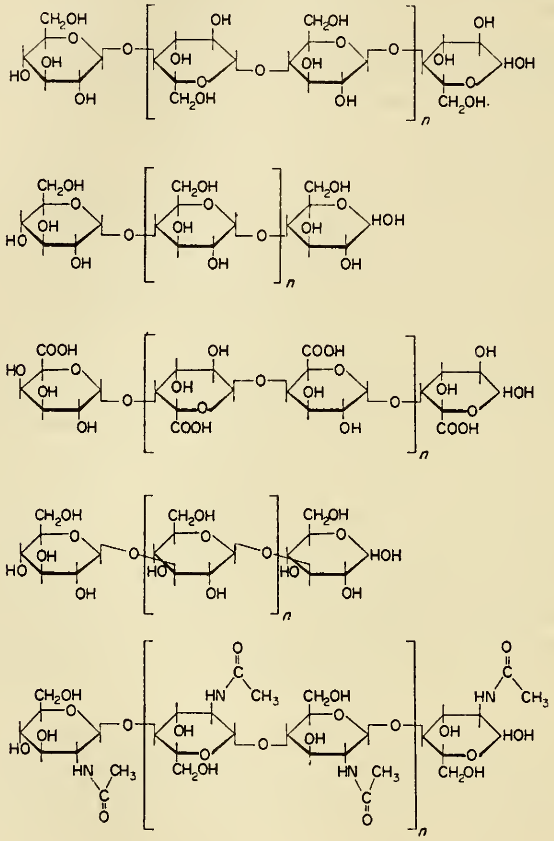


FIG. 7. Structural formulas for some common homopolysaccharides. For cellulose, $n = 2 - 3 \times 10^3$; for amylose, $n \simeq 300$; for pectic acid, $n = 25—100$; for for laminaran, $n \simeq 20$ (?); for chitin, $n = 10^3$.

Paper chromatography and paper electrophoresis of carbohydrates are reviewed in the following manuals, Block *et al.* (1958), Brimley and Barrett (1953), and Cramer (1954). Special reviews of paper (Kowkabany, 1954) and column (Binkley, 1955) chromatography of carbohydrates have also been published. Ion-exchange methods are discussed by Samuelson (1953). A very useful and comprehensive book covering all aspects of chromatography is that by Lederer and Lederer (1957).

Carbohydrates in Living Organisms

Before discussing the occurrences of carbohydrates in "ecological" and fossil material, it is desirable to outline the different types of carbohydrates that are found in living organisms. The carbohydrates of angiosperms and chordates have been most thoroughly investigated. With occasional exceptions, those of the more "primitive" organisms have received little attention. It is often difficult to assert the identity of similar carbohydrates found in two or more gross taxonomic groups, especially in the case of the polysaccharides. Polysaccharides which seem to be similar in structure and chemical properties cannot be assumed to be identical in all respects. Minor differences, not revealed by current methods of analysis, may always be present.

A tabular summary of the main carbohydrates found in different plant phyla is given in Table 1. The list was compiled from information given by Fogg (1953, 1956), Percival (1950), Bonner (1950), Mori (1953) and Pigman (1957) to which reference can be made for further details. There are many complex mucilages and gums in both plant and animal tissues whose chemical natures are too poorly known to permit taxonomic comparisons.

TABLE 1.
Reserve and Structural Carbohydrates in the Plant Kingdom

Phylum	Reserve Carbohydrates	Structural Carbohydrates
Cyanophyta	Myxophycean starch (a glucan)	Amylopectins*, gums, cellulose*
Rhodophyta	Floridoside, mannoglyceride, floridean starch (α-1:3-glucan)	Agars, cellulose, xylan*
Phaeophyta	Laminaran (β-1:3-glucan)	Alginic acid, fucoidin, cellulose
Chrysophyta		
Xanthophyceae	?	Cellulose*, chitin(?)*
Chrysophyceae	Leucosin	Pectins(?)
Bacillariophyceae	Leucosin(?)	Polyglucuronide*
Pyrrophyta		
Cryptophyceae	Cryptophycean starch (a glucan)	Cellulose(?)
Dinophyceae	Dinophycean starch	Cellulose
Euglenophyta	Paramylum (a glucan)	?
Chlorophyta	Starch (a glucan)	Cellulose, pectins*
Bacteria	Glycogen (a glucan)	Glucans, fructans, polyuronides, etc.
Fungi	Glycogen (a glucan)	Chitin, cellulose
Embryophyta	Starch (a glucan) Inulin (a fructan)*	Cellulose, pectins, Mannans, xylans, arabans, etc.

* Indicates occurrence in a single species or a few species examined.

These are not listed in Table 1. The structural formulas of some of the better known homopolysaccharides are illustrated in Fig. 7.

With Table 1 as background it is possible to consider some aspects of the occurrence of carbohydrates in members of the major plant and animal phyla dealing first with low molecular weight constituents, secondly with structural (i.e. cell wall) carbohydrates, and thirdly with reserve (i.e. storage) carbohydrates.

Bidwell *et al.* (1952) and others have studied the occurrence of free sugars in members of various plant phyla. Sucrose, glucose and fructose are the main sugars found in the free state, occurring mainly in green tissues. The total free sugar content of green algae (Chlorophyta) and green tissues of higher plants (both the bryophytes and tracheophytes) averages 0.3% of the fresh weight (Bidwell *et al.*, 1952). In algal groups other than the Chlorophyta, the concentrations of free sugars are from 1/10th to 1/100th of this value. Trehalose is a common disaccharide in yeasts, blue-green algae (Cyanophyta), and some red algae (Rhodophyta), but it has not been found elsewhere in the plant kingdom in more than trace quantities. The polyhydric alcohol, mannitol, occurs in high concentration in the brown algae (Phaeophyta), amounting to 5% of the dry weight of *Ascophyllum nodosum* and *Fucus serratus*, and even up to 25% of the dry weight in some species of *Laminaria* at certain times of the year. Mannitol replaces sucrose in the brown algae as the first sugar derivative produced by photosynthesis. Some, but not all, of the red algae contain dulcitol and sorbitol. Chemical combinations of galactose and mannose with glycerol occur in the red algae in the form of the glycerides, floridoside, and mannoglyceride, respectively.

Structural carbohydrates are those that make up the cell wall or form intercellular or capsular (in the case of micro-organisms) material. Cellulose is the main structural carbohydrate in the plant kingdom. In fact, it is often stated that cellulose is the most abundant carbohydrate on the surface of the earth. Although this is probably true, it should be noted that cellulose has not been detected in diatoms (one of the dominant plant forms of the sea), and that it is outweighted by other carbohydrates in the brown and red seaweeds. Cellulose is a linear polymer of β-D-glucopyranose units linked 1:4 with chain lengths of 2000–3000 glucose units. The identity of brown algal cellulose to cellulose of higher plants has been shown by X-ray and chemical evidence (Percival and Ross, 1948). In the brown algae, cellulose comprises 2–15% of the dry weight of the plant. In woody tissues of higher plants about one-half of the dry weight is cellulose. Lichenan (=lichenin), a low-molecular weight glucan of the cellulose type, has been isolated from Iceland moss (a lichen). A similar compound occurs in oats. The cell walls of fungi may be composed of either cellulose or chitin, the two not usually occurring together according to Frey (1950).

Two apparently unique polysaccharides occur in brown seaweeds: alginic acid and fucoidin. Alginic acid is a linear β-1:4-mannuronan that occurs in the cell wall in the form of calcium and magnesium salts (algin). Fucoidin has a complex structure, but is mostly a monosulfated fucan with the predominant glycosidic links α-1:2. Red seaweeds may have agars as their structural carbohydrates. The agars of red algae are polygalactose sulfates, but the sulfur content is far lower than in fucoidin, amounting to only 0.5% or less.

A number of different pectin-type compounds are present in plants. In higher plants the term "pectins" refers to a mixture of methyl esters of pectic acid (a polymer of D-galacturonic acid), a galactan, and an araban. The pectins occur mostly as intercellular material. Analysis of a "pectin-like" capsular material of the diatom *Navicula pelliculosa* showed that it was a polyglucuronide (Lewin, 1955).

Bishop *et al.* (1954) isolated a polysaccharide from *Anabaena cylindrica* (Cyanophyta) which yielded on hydrolysis glucose, xylose, galactose, rhamnose, arabinose and glucuronic acid in the proportions 5:4:1:1:1:4.

The main sugar components (exclusive of uronic acids) of some representative woods are listed in Table 2. Softwoods have a relatively high content of mannans and galactans, whereas hardwoods are rich in xylans.

TABLE 2.

Sugars released by Acid Hydrolysis of Different Woods. The Data are given as a Percentage of the Total Polysaccharide, excluding Uronic Acid Content

From the data of Gustafsson, Pettersson and Lindh as summarized by Polglase (1955)

Species	Glucan %	Mannan %	Xylan %	Galactan %	Araban %
Softwoods					
Spruce (*Picea excelsa*)	65.5	16.0	9.0	6.0	3.5
Pine (*Pinus sylvestris*)	65.0	12.5	13.0	6.0	3.5
Cedar (*Juniperus communis*)	61.0	14.0	11.0	13.5	0.5
Hardwoods					
Birch (*Betula verrucosa*)	58.5	0.5	39.0	1.5	0.5
Birch (*Betula pubescens*)	55.0	2.5	39.0	1.0	2.5
Oak (*Quercus ruber*)	68.5	2.0	26.0	2.5	1.0
Ash (*Fraxinus excelsior*)	60.0	2.5	32.0	3.0	2.5

Starch is the characteristic reserve polysaccharide of higher plants. It is deposited in leaves during photosynthesis and disappears during darkness. Starch is deposited in the form of granules containing two different polysaccharides: (a) amylopectin, a branched glucan; and (b) amylose, a linear glucan. These occur in the ratio of about four to seven amylopectins per amylose. The amylopectin part of the starch grain has an average chain length of 20–26 glucose units and a molecular weight of over 10^5. In some angiosperms (Compositae and Gramineae), low molecular weight fructans, such as inulin (a β-1:2-fructan), occur as reserve polysaccharides. Green-algal starch appears to be identical in composition to that from higher plants, however, in other algal groups the reserve polysaccharides differ structurally from those of the green algae and higher plants. The starch of Cryptophyceae shows the greatest resemblance to that of higher plants, and contains amylose and amylopectin in approximately equal amounts. On the other hand laminaran (= laminarin) of the brown algae is a linear β-1:3-glucan. At certain times of the year, laminaran may form 50% of the dry weight of fronds of *Laminaria saccharina*. Floridean starch of the red algae is an α-1:3-glucan. The paramylum granules deposited by photosynthesizing *Euglena* cells consist of a glucan of unknown constitution. The reserve polysaccharides of other algae have received little attention from chemists. Myxophycean starch and leucosin are assumed to be carbohydrates from their biological behaviour.

Bacteria produce a variety of polysaccharides that occur as capsular material around the cell wall. Glucans, fructans, uronic acid containing gums and mucilages, etc., are not uncommon. Some of these bacterial polysaccharides appear to exert an important influence on soil texture by binding soil particles together. The presence of aminopolysaccharides in bacteria and other organisms has been reviewed by Kent and Whitehouse (1955).

Carbohydrates form a smaller percentage of the organic matter of animals than they do of plants, being diluted in animals by proteins. Glycogens are the main reserve polysaccharides of the animal kingdom. The glycogens are branched glucans, like the amylopectin part of starch, but with shorter average chain lengths (usually 12 in glycogen as compared to 20–26 in amylopectin) and higher molecular weights (10^6–10^7 in glycogen as compared to 10^5–10^6 in starch). Glycogens have been detected in protozoans, flatworms, nematodes, annelids, molluscs, and chordates.

Although cellulose is characteristically a plant polysaccharide, it is interesting to note its presence in tunicates (sea-squirts), and in collagenous connective tissues of cows, and probably other mammals as well (Hall *et al.*, 1958). Chitin (poly—N-acetyl-D-glucosamine) is a major component of the exoskeletons of certain members of the Arthropoda, notably in the classes Crustacea, Onychophora, Insecta, Myriapoda and Arachnida where it comprises 2–45% of the organic matter in the exoskeleton (Kent and Whitehouse, 1955). Chitin is not the strengthening element of the arthropod exoskeleton. In the Crustacea the strengthening material is $CaCO_3$, whereas it is scleroprotein in the other classes.

Hyaluronic acid (a polymer of N-acetyl-D-glucosamine and glucuronic acid) is present in vertebrate connective tissues along with chondroitin sulfates (sulfate-containing polymers of N-acetyl-D-galactosamine and glucuronic acid). Other nitrogen- and sulfur-containing polysaccharides occur as mucilages in the gut and other parts of the body.

Many other polysaccharides occur in animal tissues, eggs, excreted slimes, and so on, but reference to them is beyond the scope of this chapter. Further information can be found in those references that deal with the chemistry and biochemistry of the carbohydrates.

General Remarks on the Geochemistry of the Carbohydrates

It must be stressed that laboratory data on the chemical composition of micro-organisms may be misleading when applied to the same organisms in their natural habitats. It is characteristic of organisms that they adapt themselves to their environment. New enzyme systems may be developed with consequent changes in the chemical composition of the body. A striking case in point has recently come to light (Lewin, 1955). Under healthy culture conditions the diatom *Navicula pelliculosa* is not encapsulated, but when the cells are maintained in a non-dividing state (as by poor nutrient conditions) a polyglucuronide capsule is elaborated around the siliceous test. Plant physiologists are prone to work with healthy cells in pure culture, whereas in nature phytoplankton cells may not be in a healthy condition at all times of the year and, in any case, occur as mixed populations in the presence of bacteria. The value of studying single species cultures in the laboratory is not to be questioned; only the extent to which such data are applicable to field populations.

Although there are marked differences between the geochemistry of inland and marine waters, it is convenient to discuss some aspects of their organic geochemistry together, partly because of the paucity of the data, but also because of the similarity of aquatic environments in their high water content. The presence of excess water indirectly retards the biological decomposition of many organic compounds as evidenced by the rapid decomposition of woody tissues in normal soils as compared with flooded soils.

Freshwater and Marine Seston

The term seston is used to refer to the particulate matter of natural waters; it consists of living organisms (plankton) and dead materials (detritus). The most extensive body of data on the chemical composition of sestonic organic matter is that given for Wisconsin lakes by Birge and Juday (1926, 1934). Crude protein (nitrogen content × 6.25, assuming all the nitrogen to be in the form of proteins containing 16.0% nitrogen), fat, and "carbohydrate," were estimated from measurements of organic carbon, total nitrogen, and the weights of the ether extracts. The mean "carbohydrate" content of the seston of Wisconsin lakes was found to be 59% of the dry weight. This value must be maximal since it is based on the assumption that all that is not fat and not crude protein is carbohydrate. Brandt (1898) found an average of 42% "carbohydrate" in marine seston sampled over the year. Trask (1937) states that 63–85% of the dry weight of marine seston is composed of non-nitrogenous organic material. Kusnetzov and Kusnetzova (1935) reported that one sample of seston from Lake Beloie, Russia, contained 10.5% cellulose and a total of 31.5% sugars, hemicelluloses, and pentosans. Raymont and Krishnaswamy (1960) and Raymont and Conover (1961) have analyzed a variety of *marine zooplankters* for easily hydrolyzable carbohydrates based on the pink color produced after boiling samples for 5 min in 25% H_2SO_4. The following genera were studied: *Calanus*, *Meganyctiphanes*, *Thysanoessa*, *Nematoscelis*, *Neomysis*, *Paraeuchaeta*, *Euthemisto*, *Pleuromamma*, *Hyperea*, *Conchoecia* and *Pleurobrachia*. The carbohydrate contents were generally in the range of 0.1 to 0.2% of the fresh weight with extremes ranging from 0.04 to 0.60%. Freshly caught *Calanus finmarchicus* contained 0.11 to 0.13% carbohydrate on a wet basis, corresponding to about 0.4% of the dry weight.

The nature of sestonic carbohydrates has been determined only in a few instances. Schuette (1918) found small amounts (0.6% of the dry weight) of reducing sugars in one sample of lake seston, but failed to detect reducing sugars in other samples. More recently, Whittaker and Vallentyne (1957) identified sucrose, maltose, glucose, and fructose in samples of lake seston using paper chromatography for separation and semi-quantitative estimation. Free sugars composed 0.3% of the dry weight of floating (partially decomposed) seston that had accumulated in a bay under favorable wind conditions. A single sample of open-water seston from the same lake contained 4.2% free sugar, mostly glucose. The presence of maltose, which is not a normal free sugar in plants, was taken as an indication of the breakdown of starch-like polysaccharides in the seston.

Parsons and Strickland (1962) analysed the detritus present in 150-liter samples of subsurface waters from the northeastern Pacific Ocean. The concentrations of detrital carbohydrates (determined by reaction with anthrone) in three samples at 1500 m depth were 21, 25 and 27 mg per m^3 of water. More complete data down to 3000 m depth are given in their paper. Approximately 70% of the carbohydrate consisted of crude fiber. Glucose, galactose, mannose, arabinose and xylose were liberated by hydrolysis of the samples with glucose accounting for approximately half of the sugars found. Neither glucosamine nor hexuronic acid was detected in hydrolysates of detrital material from any depth.

Hough *et al.* (1952) examined seston samples from Windermere, England, for polysaccharides. A glucan of the amylopectin type was isolated from a sample of seston rich in *Oscillatoria* (Cyanophyta), and a complex polysaccharide (containing xylose, galactose, rhamnose, glucuronic acid and glucose) from seston rich in *Nostoc* (Cyanophyta). The *Nostoc* gum is apparently similar to a gum produced by *Anabaena cylindrica* in pure culture (Bishop, Adams and Hughes, 1954).

Pentosans and methylpentosans have been detected in both marine and freshwater seston (Wells and Erickson, 1937; Skopintsev, 1948) in concentrations of a few percent of the sestonic organic matter. According to Skopintsev (1948) methylpentosans replace pentosans during the laboratory decomposition of freshwater seston.

Inasmuch as chitin occurs in fungi and in crustacean zooplankters, it can be expected to form part of the sestonic carbohydrate. Chitin has been identified in both freshwater and marine seston on the basis of color reactions and proximate analysis (Brandt, 1898; Schuette, 1918; Waksman *et al.*, 1933). Krause (1959) found 3.8–7.7% chitin in the dry matter of freshwater zooplankters, with only slightly lower values for the same zooplankters after 30 days aerobic or anaerobic decomposition. Chitin evidently decomposed at about the same rate as the total dry matter.

"Dissolved" Substances in Fresh and Marine Waters

It is important to realize that about five-sixths of the total organic matter in a unit volume of lake water will pass through a bacterial filter; only about one-sixth occurs in the form of seston (Birge and Juday, 1934; Krogh and Lange, 1931). The same is true of the marine environment (Fox *et al.* 1952). Representative data are given in Table 3 for the proximate chemical composition of the colloidal and dissolved organic matter fractions from Furesee, a Danish lake. Birge and Juday (1934) found that the "dissolved" organic matter in clear-water lakes of Wisconsin contained an average of 73% "carbohydrate"; values up to 90% were found in waters from bog lakes. The "dissolved" fraction was that which did not settle on strong centrifugation. It is not yet clear as to what types of compounds are present in the "carbohydrate" fraction of the dissolved organic matter. Goryunova (1954) recently claimed that the dissolved organic matter of lake water actually is rich in polysaccharides. Hutchinson (1957) has authoritatively reviewed studies on the nature of the "dissolved" organic matter of lake waters.

TABLE 3.

Proximate Chemical Composition of Seston, Colloidal and Soluble Organic Matter from Furesee, Denmark

From Krogh and Lange, 1931.

Sample	Concentration mg/l.	Protein %	Fat %	Carbohydrate %
Sestonic organic matter	1.56	53.2	9.9	36.9
Colloidal organic matter	0.67	41.5	11.7	46.8
Soluble organic matter	8.8	37.5	—	62.5

The only specific carbohydrates that have been identified in filtered waters are dehydroascorbic acid, which Wangersky (1952) recovered in traces from sea water, and sucrose and glucose, which occur in trace amounts in filtered lake water (Vallentyne and Whittaker, 1956). Other types of carbohydrate have been estimated on the basis of color reactions, but their exact nature is unknown. Wangersky (1952), for example, reported the presence of a "rhamnoside" in Gulf of Mexico waters in concentrations up to 100 mg/l. Collier *et al.* (1950, 1953) found somewhat lower concentrations of carbohydrates (or compounds associated with carbohydrates) in the same waters. These materials increased the pumping rates of oysters. Lewis and Rakestraw (1955) applied colorimetric methods (reaction with anthrone or N-ethylcarbazole) to Pacific waters and found very low carbohydrate concentrations (0.1–0.7 mg/l. in terms of sucrose equivalents); higher concentrations (up to 8 mg/l.) occurred in the region of kelp beds. According to May (1960), dissolved carbohydrates (measured by reaction with N-ethylcarbazole) can be determined up to 7 weeks after collection if seawater samples are stored at —18°C.

Some algae liberate large amounts of polysaccharide to the culture medium under normal culture conditions. This has been shown for *Chlamydomonas* spp. and some other green algae by Lewin (1956), for *Anabaena cylindrica* (Cyanophyta) by Bishop *et al.* (1954), and for *Prorocentrum* (Dinophyceae) by Collier (1958). In the case of *Chlamydomonas*, 4–57% of the synthesized organic matter was liberated as extracellular material, of which carbohydrates formed a considerable part. These laboratory observations indicate a possible counterpart under environmental conditions.

It is usually assumed that the dissolved organic matter in both fresh and marine waters is biologically inert; however, Waksman and Carey (1935) demonstrated that at least 25% of the dissolved organic matter in sea water is subject to rapid bacterial decomposition in the laboratory. The rates of breakdown and synthesis of various fractions of the dissolved organic matter under environmental conditions have never been determined, though they should be amenable to attack using isotopes. The ecological importance of dissolved organic matter has been reviewed by Saunders (1957). Apart from the possible role of carbohydrates in affecting the pumping rates of oysters (Collier *et al.*, 1950, 1953), no specific ecological roles have as yet been clearly demonstrated for dissolved carbohydrates.

Freshwater Sediments

The organic matter of sediments is derived mostly from the partially decomposed remains of plankters, both plant and animal; however, in shallow waters and in lakes of small area the sedimentary organic matter may originate from macroscopic aquatic and terrestrial vegetation. The lighter and smaller organisms or broken fragments of larger organisms tend to accumulate in the deeper parts of the basin where current action is low.

Data on the proximate chemical composition of fresh-water sediments (lake muds and peats) are given in Table 4. In general, the organic matter of *Sphagnum* peat is rich in cellulose relative to lowmoor peats (*Scirpus* peat and *Phragmites* peat) and lake muds. Hemicelluloses (of an unknown nature) are present in all.

TABLE 4.

Major Organic Components of Lake Sediments and Peats

Data for lakes from Kusnetzov and Kusnetzova (1935), for peats from Waksman (1952). Data expressed as a percentage of the total organic matter.

Sample	Depth below mud surface	Ash content of the dry sediment	As % of total organic matter: Sugars, pentosans and hemicelluloses	Cellulose	Crude protein	Lignin + humus
Lake Beloie	0–5 cm	10.66	7.90	7.21	14.18	21.53
	25–40 cm	9.78	8.34	5.45	13.56	24.08
Lake Glubokoie	0–5 cm	11.16	1.16	2.51	5.98	14.8
	10–15 cm	10.01	0.92	1.53	4.39	16.8
Lowmoor peat, N.S.	Sub-surface	13.2	11.9*	0.0	25.9	44.2
Sawgrass peat, Fla.	Sub-surface	10.0	7.1*	0.3	25.7	51.3
Sphagnum peat, Ger.	Sub-surface	1.7	17.2*	19.8	5.3	34.7
Sphagnum peat, Maine	Sub-surface	1.8	21.3*	16.5	5.8	25.9

* Hemicelluloses only.

Until recently it has been assumed that sediments, because of their high bacterial content, should not contain simple nutrients such as free sugars. Contrary to this expectation, Vallentyne and Bidwell (1956) and Whittaker and Vallentyne (1957) found free sugars in all freshwater sediments that contained organic matter, the amounts of sugars ranging from 10 to 3000 mg/kg of organic matter in the sediment. The following sugars were identified on paper chromatograms of ethanolic extracts of sediments: sucrose, maltose, glucose, fructose, galactose, arabinose, xylose, ribose, and an unknown which may be a trisaccharide. Maltose, glucose, and sucrose occurred most frequently and in the largest amounts. The pentoses were found only occasionally, and then only in traces.

Whittaker and Vallentyne (1957) demonstrated that the sedimentary sugars are quantitatively extracted with either cold or boiling 70% ethanol but not with water. The sugars are quantitatively associated with the particles of the sediment: the interstitial water of the mud is lacking in free sugar. A pronounced decrease in free sugar content with depth was found in two cores of near-surface sediment. The data for one of these cores are presented in Table 5.

In many cases the amount of free sugar found in the sediments is too large to be accounted for on the assumption that it is all present in living

TABLE 5.

Sugars extractable with 70% Aqueous Ethanol from Core Samples of Mud from Lake Opinicon, Ontario

Depth (cm)	Maltose	Sucrose	Glucose	Total	Sugar in pore H_2O (ppm H_2O)	Ignitable matter %	H_2O in sediment %
0–5	1.6	0.2	1.3	2.9	<0.1	51.9	97.8
5–10	1.0	0.1	0.90	1.9	<0.1	52.1	96.9
10–15	0.95	0.00	0.46	1.4	<0.1	51.5	96.2
20–25	0.81	0.00	0.57	1.4	<0.1	51.5	95.9
30–35	0.34	0.00	0.17	0.5	<0.1	52.5	95.9
40–45	0.04	0.00	0.04	0.08	<0.1	54.8	95.9

Depths refer to distance below the mud–water interface. Concentrations as grams of sugar per kilogram of sediment ignitable matter. Data from Whittaker and Vallentyne (1957)

micro-organisms in the mud. Some other mechanism of binding must be present, but that mechanism is not yet known. Two different origins for the sugars have been postulated (Whittaker and Vallentyne, 1957): (a) from polysaccharide breakdown either in the mud or in seston; and (b) directly from the free sugars of living plants. Since maltose is not a normal free sugar in plants, it must originate by the first mechanism. Sucrose, on the other hand, is a normal free sugar in green tissues, and would be difficult to account for by polysaccharide breakdown. Glucose and fructose might have originated by either route. It is interesting to note that Pochon and Chalvignac (1951) claim that starch breakdown in the soil proceeds in two stages: enzymic hydrolysis of starch to dextrins, maltose and glucose by one set of bacteria, followed by subsequent fermentation of sugars by other bacterial species. If this were true in lake sediments, it might provide an explanation for the occurrence of maltose and glucose, however, the original suggestion for the soil bacteria needs further documentation.

The polysaccharides of freshwater sediments have not been studied in detail. Cellulose is known to be present from proximate analyses. Lieske and Winzer (1931) found a decrease in the cellulose: lignin ratio from 1.29 in living *Eriophorum* to 0.73 in *Eriophorum* peat 1.5 m below the surface of the deposit. The only purified polysaccharide that has been isolated from freshwater sediments is the cellulose that Hess and Komarewsky (1928) prepared from *Sphagnum* peat. This preparation was shown to be devoid of methoxyl groups, to agree in carbon and hydrogen content with standard cellulose, and to form an acetate with the same specific rotation as cellulose acetate. Unfortunately, the molecular weight of the cellulose was not estimated.

Theander (1952) hydrolyzed *Sphagnum* peat under conditions that would hydrolyze cellulose. The fermentable reducing substances liberated by this treatment formed 28% of the total organic matter of the peat. Galactose, glucose, mannose, arabinose, xylose, and rhamnose were identified by paper chromatography. A later study (Theander, 1954) showed that while holocellulose formed 83–86% of the *Sphagnum* organic matter, it formed only 51–64% of the organic matter of *Sphagnum* peats up to 4800 years old. Fructans were particularly labile as evidenced by their presence in *Sphagnum*, but not in *Sphagnum* peat estimated to be 200–400 years old. The greatest depth-decrease in carbohydrates occurred at the junction between the living plants and the peat. The sugars previously identified were again reported, plus galacturonic acid and an unidentified monomethyluronic acid.

Duff (1952) obtained water-soluble polysaccharides from peats and soils, which were noted to contain L-fucose. Black *et al.* (1955) used acid extraction and ethanol and acetone precipitation to obtain a polysaccharide fraction from *Sphagnum* peat. The equivalent weight of the polysaccharide preparation was 3150, assuming one uronic acid moiety per molecule. Hydrolysis liberated glucose, mannose, xylose, galactose, and an unidentified uronic acid in the proportions 12:3:2:1:1.

Pentoses may occur in peats in the form of nucleotides (Bottomley, 1917) but the quantities are unknown. Neither hexosamines nor chitin have been detected in lake sediments, though they must certainly be present.

It may be of interest to know that cotton (i.e. cellulose) strings are decomposed more quickly than silk (i.e. protein) strings when both are inserted at various depth intervals into cores of lake sediment (Züllig, 1956). The decomposition of both types of string was most active in surface sediments.

Sedimentary rocks of freshwater origin have been analysed for carbohydrates. Whittaker and Vallentyne (unpublished) analysed an organic-rich sample of Eocene Green River Shale for sugars liberated by hydrolysis but none were found by paper chromatography. Under the conditions of analysis the limit of detection was 2 mg of any one sugar per kilogram of rock. Using larger samples, Palacas (1959) found traces (< 1 mg/kg) of glucose in hydrolysates of two samples of Green River Shale.

Marine Sediments

Trask (1937) used 40% crude protein, 1% lipid, and 47% non-nitrogenous compounds (one-fiftieth of which was listed as cellulose) for the composition of the organic matter of an average marine sediment. Much variation in the composition of the sedimentary organic matter can be expected depending on the depth of the water column in which sedimentation took place.

Qualitative paper chromatographic evidence of free sugars in ethanolic extracts of marine sediments from the Carribean has been reported by Plunkett (1957). Sucrose, glucose, fructose, galactose, arabinose and xylose were identified, but the amounts not stated.

Polysaccharides have not been isolated as such from marine sediments, however, Wells and Erickson (1937) reported the presence of pentosans and methylpentosans in a shallow water marine mud, and Shabarova (1955a) has more recently presented quantitative data on carbohydrates in sediments of marine and inland seas. Shabarova's data are summarized in Table 6. The large amount of non-hydrolyzable matter in most of the samples is striking, as is also the low amount of carbohydrate in the deeper marine and saline sediments studied.

Shabarova (1955b) examined a middle Miocene petroleum sand for carbohydrates but failed to detect any sugars in a hydrolysate of the

Table 6.

Proportion of Individual Components in the Organic Matter of Recent Sediments

Expressed as a percentage of the total organic compound found.

A = argillaceous; B = black mud; D = diatomaceous; G = grey mud; S = silty

Data from Shabarova (1955a)

Sampling Site	Sediment type	Total organic compounds determined (% of dry wt.)	Lipids	Protein	Carbohydrates	Unhydrolyzable residue	Total hydrolyzable compounds
Continental shelf, eastern U.S.S.R.							
988 m depth	AD	4.57	4.38	6.96	0.74	87.97	12.03
1497 m depth	AD	8.48	5.91	7.75	traces	87.34	12.66
Black Sea							
coastal mud	G	7.37	7.75	56.31	10.83	24.69	75.31
50 m depth	AG	3.89	2.55	9.41	0.00	88.04	11.96
220 m depth	AB	4.89	2.33	10.73	0.00	86.84	13.16
294 m depth	AB	8.05	2.09	3.17	0.00	94.74	6.26
Caspian Sea							
18 m depth	AS	4.89	8.70	7.48	1.03	82.79	17.21
18 m depth	AG	4.56	7.68	9.43	1.54	81.35	18.65
White Sea							
90 m depth	G	2.41	5.60	11.15	5.25	78.00	22.00
Kura River Delta							
advance delta	AG	4.69	2.15	7.88	0.00	89.97	10.03
Lake Biserovo							
unstated depth	B	35.77	6.90	34.85	33.15	25.10	74.90

TABLE 7.

Sugars in Acid Hydrolysates (72% *H_2SO_4 for* 2 *hours at* 4°*C followed by* 1N *H_2SO_4 for* 10 *hours at* 100°*C*) *of a Sediment Core from the Santa Barbara Basin, Calif.* (*mg/g dry weight*).
Data from Prashnowsky *et al.* (1961).

Number	1	2	3	4	5	6	7	8	9	10	11	12
Depth, cm	0–10	10–20	20–30	30–40	40–50	50–60	90–100	150–160	200–210	260–270	310–320	360–370
Galactose	0.26	0.28	0.53	0.36	0.31	0.37	0.63	0.14	0.18	0.01	0.18	0.03
Mannose	0.07	0.13	0.22	0.33	0.28	0.17	0.57	0.01	0.35	0.02	0.19	0.01
Glucose	0.22	0.16	0.17	0.16	0.31	0.45	0.21	0.02	0.12	0.03	0.01	0.03
Rhamnose	0.06	0.02	0.11	0.40	0.16	0.21	0.13	0.04	0.05	0.05	0.09	0.08
Ribose	0.06	0.13	0.52	0.09	0.10	0.24	0.28	0.04	0.26	0.06	0.09	0.06
Xylose	0.10	0.24	0.28	0.16	0.16	0.17	0.28	0.03	0.01	0.23	0.12	0.01
Arabinose	0.13	0.14	0.11	0.23	0.18	0.29	0.07	0.02	0.03	0.27	0.22	0.02
Total	0.89	1.10	1.94	1.73	1.50	1.90	2.17	0.30	1.00	0.67	0.90	0.24
Organic carbon	24.1		29.9			30.1	30.0	27.0	24.5	26.0	20.7	24.5
Total organic matter	41.0		50.8			51.2	51.0	45.9	41.6	44.2	35.2	41.6
% Sugars in total organic matter	2.2		3.4			3.7	4.3	0.7	2.4	1.5	2.6	0.6

bitumen-free sand. It is noteworthy that amino acids were present in the hydrolysate. Swain, Blumentals and Prokopovitch (1958) report that reducing substances (assumed to be related to carbohydrates) are present in hydrolysates of Precambrian sedimentary rocks. Palacas, Swain and Smith (1960) found glucose (0.14–1.3 mg/kg rock), arabinose, xylose, and some other sugars in hydrolysates of sedimentary rocks of Ordovician to Miocene age. D-glucose was isolated from Paleozoic black shales. In a separate study of Jurassic rocks of the Gulf of Mexico region, Swain (1961) identified furfural and 5-hydroxymethylfurfural in HCl distillates of some rock samples.

Data on the sugars released by acid hydrolysis of marine sediments from the Santa Barbara Basin off the coast of California are given in Table 7 as reported by Prashnowsky *et al.* (1961). In addition to the sugars listed, traces of fucose were present in hydrolysates of all samples. The lack of a great preponderance of glucose in the hydrolysates of these sediments was thought to reflect the lower concentrations of cellulose present in marine biocoenoses as compared to terrestrial biocoenoses (Prashnowsky *et al.*, 1961). Comparable data are given in Table 8 for sugars released by acid hydrolysis of sediments from one of the preliminary Mohole cores taken from the eastern Pacific. It is of interest that the lowermost sample at 138 m depth of sediment still contained carbohydrate material in spite of its great age (certainly pre-Pleistocene and possibly extending into the Miocene).

TABLE 8

Hexoses and Pentoses in Acid Hydrolysates of Selected Samples of a Preliminary Mohole Core from the Pacific Ocean (E. T. Degens, unpublished). Concentrations are expressed as mg of sugar per kg dry weight of sediment. Hydrolysis with 72% H_2SO_4 for 2 hrs at 4°C followed by 1N H_2SO_4 for 10 hours at 100°C.

Sample	EM 7–7	EM 5–T	EM 5–B	EM 9–1	EM 8–11	EM 8–12	EM 8–14	EM 8–15
Depth (m)	0	0.3	1.5	44	101	110	129	138
Galactose	75.7	70.7	32.3	tr	1.6	3.8	2.5	4.2
Glucose	56.0	29.2	13.7	1.9	3.3	6.3	3.3	4.6
Mannose	40.0	27.2	8.3	—	2.7	6.7	3.8	8.6
Rhamnose	90.0	88.5	tr	—	tr	0.4	0.4	1.2
Arabinose	58.3	22.4	13.5	—	0.6	2.7	0.7	1.8
Xylose	55.3	37.2	19.8	—	1.1	1.4	1.6	2.8
Ribose	36.3	2.1	tr	—	0.6	tr	0.3	tr
Total sugar	411.6	277.3	87.6	1.9	9.9	21.3	12.6	22.2
Organic–C (%)	0.43	0.46	0.40	0.41	1.40	0.80	1.15	3.80
Sugar as % of org–C	3.8	2.4	0.9	0.02	0.03	0.1	0.04	0.02

Soils

The organic matter (= humus) of soils has been studied for over a hundred years. It is well known that the organic matter content of soil is important in determining the ability of the soil to promote plant growth. Much of the early work on soil organic matter was concerned with elucidating the structures of humic, hymatomelanic, and fulvic acids, and other soil organic matter fractions. These fractions are removed from the soil by extraction with dilute (2%) NaOH. Humic acid is the alcohol-insoluble part of the fraction precipitated on neutralization of the alkaline extract; hymatomelanic acid is the alcohol-soluble fraction of that precipitate; and fulvic acid is the fraction not precipitated on neutralization. These "acids" are not, as their names imply, separate chemical substances, but rather, are complex mixtures of organic and associated inorganic materials. It is useful to differentiate between humic (humic acid, etc.) and non-humic (carbohydrates, proteins, etc.) substances in soils.

Between 1905 and 1915, Shorey isolated a number of pure organic compounds from different soil organic matter fractions. His investigations, undertaken at a time when analytical methods were quite primitive, can only be described in superlatives. Following the development of chromatographic methods within the last ten years, there has been renewed interest in characterizing soil organic matter in terms of discrete chemical compounds. Studies on soil organic matter have been summarized in book form by Kononova (1961). Mehta, Dubach and Deuel (1961) have also prepared a valuable and succinct review of recent studies on soil carbohydrates.

Representative data on the proximate composition of organic matter from different soils are given in Table 9. There are pronounced depth-decreases in the organic matter content of soils, and also in the percentage of carbohydrates in a given weight of organic matter. Free sugars have recently been identified in aqueous extracts (after ether extraction) of the *F*-layer (uppermost) of a pine podzol by Alvsaker and Michelson (1957). Glucose, arabinose, fructose, xylose, galactose and ribose were identified in concentrations of 2.2, 0.4, 0.3, 0.3, 0.2 and <0.01 mg/g of soil organic matter.

A number of workers have attempted to isolate polysaccharides from soils. Forsyth (1947, 1950) extracted soils with acid (pH 3) and passed the extract over animal charcoal. Elution from the charcoal with acetone failed to remove any carbohydrates, but subsequent elution with water removed a polysaccharide fraction that could be precipitated by the addition of acetone. The polysaccharides so isolated from different soils were found to be similar in optical rotation ($[\alpha]^{22}_{D} = -2^\circ$ to -10°) and in sugars recovered on hydrolysis (galactose, glucose, mannose, xylose, and glucuronic acid). Molecular weights (as determined by titration) varied from 1000 to 1300 for different soil polysaccharide preparations. From one humus-rich soil a polysaccharide was isolated which contained galactose, glucose, mannose, arabinose, xylose and an aldobiuronic acid (glucose + glucuronic acid) in the proportions 2:2:2:1:3:2. The arabinose

TABLE 9.

Composition of the Organic matter of Different Soils in Terms of the major Fractions

Data from Waksman and Hutchings (1935) expressed as a percentage of the total organic matter. The data for hemicelluloses really refer to reducing substances in acid hydrolysates of soils.

Soil types	Horizon or depth (cm)	Hemicelluloses	Cellulose	Crude protein	Lignin	Total accounted for
Heath podzol	A_1	14.25	14.81	8.71	50.85	88.62
	A_2	5.90	5.41	9.75	45.74	66.80
	B_2	8.12	3.12	10.03	63.14	84.41
Michigan podzol	A_1	11.54	5.00	16.08	55.62	88.24
	A_2	8.18	2.10	27.82	46.32	84.12
Sassafrass loam	—	7.19	3.64	34.61	34.90	80.34
Chernozem (Texas)	0–20	1.41	5.44	44.34	35.36	86.55
	30–50	0.00	4.28	32.53	32.53	69.34
Chernozem (Oklahoma)	0–20	6.95	8.86	38.08	32.59	86.48
	20–50	3.45	4.23	41.45	35.26	84.39
Chestnut	0–15	7.15	4.82	32.70	39.95	84.62
	15–48	5.50	4.77	36.26	34.15	80.68
Serozem (Arizona)	0–15	1.14	3.20	50.22	34.76	89.32

moiety could be removed by boiling the polysaccharide for 24 hr in water. Using similar methods, Duff (1952a, 1952b) identified L-fucose and methylhexoses (probably a methylglucose and a methylgalactose) in the hydrolytic products of polysaccharides from soils and peats. Müller, Mehta and Deuel (1960) have described a method for the fractionation of soil polysaccharides on columns of DEAE-cellulose.

Whistler and Kirby (1956) extracted a Brookston-type agricultural soil with water and precipitated a polysaccharide fraction with acetone. The hydrolytic products were D-glucose, D-galactose, D-mannose, L-arabinose, D-xylose, L-rhamnose, glucuronic acid, ribose (traces), and glucosamine (traces). A highly purified polysaccharide preparation has recently been obtained from the ethanol-insoluble part of an aqueous extract of a muck soil (Clapp, 1957). The polysaccharide was shown to move as a single component on paper electrophoresis and ultra-centrifugation. Glucose, mannose, galactose and rhamnose were identified as hydrolytic products. Haworth *et al.* (1946) reported that fructans were present in soil polysaccharide fractions, however, other workers have failed to corroborate this finding.

It is doubtful that any of the above polysaccharide preparations can be considered to be a single substance. The differences noted may partly result from the presence of different polysaccharides, and partly from variations in the method of isolation. Most workers have assumed that the water-soluble soil polysaccharide preparations represent products of bacterial metabolism in the soil. It will be shown later that polysaccharides are important in causing the aggregation of soil minerals. It is, therefore, interesting to note that Stevenson and co-workers (1952) obtained an organic-clay fraction which on hydrolysis yielded galacturonic acid, xylose, ribose (traces) and glucurone (traces), in addition to amino acids.

Lynch *et al.* (1957) demonstrated that 0.5–2.0% of the weight of humic acid fractions from four soils could be accounted for as sugars released by hydrolysis. Glucose, galactose, arabinose, xylose, fucose, rhamnose, and mannose were detected in roughly that order of abundance. Other carbohydrates identified in smaller amounts by paper chromatography were ribose, glucosamine, mannitol, inositol, galacturonic acid, glucuronic acid, 2-O-methyl-D-xylose, and 2-O-methyl-D-arabinose. Forsyth (1948) reported that soil humic acid fractions may contain as much as 8–13% carbohydrates.

Pentosans appear to be common soil constituents. They were first measured in soils by Shorey and Lathrop (1910) on the basis of furfuraldehyde production with 12% HCl. These investigators isolated a pentosan yielding only xylose on hydrolysis. A comparison of diverse methods for the estimation of pentosans in soils has been undertaken by Mehta and Deuel (1960).

The first clear-cut evidence for hexosamines in soils was provided by Bremner (1950), although Shorey (1930) had previously obtained suggestive evidence for their presence. More recent work (Bremner and Shaw, 1954; Stevenson, 1954, 1957a, 1957b, 1957c) shows that aminosugars account for 5–13% of soil nitrogen. Both glucosamine and galactosamine have been found in soil hydrolysates (Adams *et al.*, 1954; Stevenson, 1954, Bremner, personal communication), but glucosamine apparently predominates. There have been reports of N-acetyl-D-glucosamine in hydrolysates of soil or soil fractions (Stevenson, 1956; Lynch *et al.*, 1957). Hydrolysis with weak acids for short periods of time may not quantitatively remove the N-acetyl groups from N-acetyl-D-glucosamine. The extent to which chitin occurs in soil has not been determined.

Martin and Shorey (1930) first demonstrated that polyuronides were present in soils. As determined by carbon dioxide production by decarboxylation of uronic acids with HCl, the carbon in uronic acids appears to account for 5–28% of the soil organic carbon (Martin and Shorey, 1930; Norman and Bartholomew, 1943), however, the decarboxylation technique yields high results. Lynch *et al.* (1957), who developed a new method for polyuronide analysis in soils, did not determine the ratio of uronic acid-carbon to total soil organic-carbon, however, they state that 90% of uronic acids in soil occur in the fulvic acid fraction. This method is based on the reaction of uronic acids with carbazole. The method has been tested by Dubach and Lynch (1959) and found to give far more satisfactory results than estimation by reaction with hot 12% HCl. The latter method gives erroneously high values for uronic acids in soil since the bulk of the CO_2 produced by reaction of soil organic matter with hot 12% HCl originates not from uronic acids but from other more labile soil constituents (Deuel and Dubach, 1958a, 1958b). This had been predicted earlier by Tyurin (1940). Forsyth (1948) suggested that polyuronides are more stable in soils than are hemicelluloses or celluloses.

Glycosides are present in soils. Shorey (1913) isolated a glycoside that yielded rhamnose (identified by its melting point and that of its phenylhydrazone) on hydrolysis, but the aglycone was not identified. Forsyth (1947) obtained suggestive evidence for the presence of phenolic glycosides in the fulvic acid fraction of soil organic matter.

Two other substances related to carbohydrates have been isolated from soils: mannitol and inositol. Mannitol was first isolated by Shorey (1913), and later by Sallans and co-workers (1937) and by Lynch *et al.* (1957). Shorey (1913) obtained evidence for the presence of inositol in soils, but he was unable to demonstrate its presence authoritatively. This has since been achieved by Sallans *et al.* (1937), Yoshida (1940), Dyer *et al.* (1940), Bower (1945), Smith (1952), Nørgaard-Pedersen (1953), and Lynch *et al.* (1957). Although there is still some question as to the manner of occurrence of inositol in soils, it seems to be present both as phytin (salts of inositol hexaphosphate) and as less phosphorylated derivatives of phytic acid.

It has been known for many years that at least two inositol isomers exist in soils in hexaphosphorylated form. One of these was identified as *myo*-inositol hexaphosphate (= *meso*-inositol hexaphosphate), while the nature of the other was until recently uncertain. Caldwell and Black (1958) made quantitative determinations of the two inositol hexaphosphates in 49 soil samples, and reported that *myo*-inositol was on the average twice as abundant as the unidentified isomer. When soils containing low amounts of inositol hexaphosphates were enriched with nutrients to encourage microbial growth over a period of a few months it was found that the proportion of the unidentified isomer increased, reaching a final concentration twice that of *myo*-inositol hexaphosphate. This indicated that the unidentified isomer was formed as a result of microbial growth. Total inositol hexaphosphate concentrations in untreated soil samples (expressed in terms of phosphorus) ranged from 4 to 98 mg P per kg of soil with an average of 39 mg of inositol hexaphosphate-P per kg of soil. Total inositol hexaphosphates accounted for an average of 17% of the organic-P of the soil, with a range from 3% to 52%. More recently Cosgrove (1962) has reported two interesting findings: (a) that *myo*-inositol hexaphosphate fractions contain 10–20% of DL-inositol hexaphosphate; and (b) that the unidentified isomer referred to above is *scyllo*-inositol hexaphosphate. This is the first time that a phosphate derivative of *scyllo*-inositol has been found in nature. The formation of both DL-inositol and *scyllo*-inositol was attributed by Cosgrove to soil microorganisms. Direct experiment showed that the DL-inositol hexaphosphate was not produced during laboratory treatment of the soil samples. It apparently occurred as such in the soil.

Nucleic acids probably occur in small amounts in soils (Wrenshall and Dyer, 1941; Anderson, 1957) either as such or as partly degraded materials. There has not been enough work done on these compounds to indicate their fate during geologic decomposition processes. According to Anderson (1958), DNA is present in humic acid precipitates of soil organic matter. RNA, if it is present at all, must be largely decomposed during alkaline extraction yielding acid-soluble products that appear in the fulvic acid fraction. In one sample of Scottish agricultural soil the humic acid fraction contained the four nitrogenous bases typical of DNA (guanine, cytosine, adenine and thymine) with G/C and A/T ratios approximately equal to unity (Anderson, 1958). These data, plus the fact that the nitrogenous bases accompanied the humic acid precipitate indicated that the bases must have occurred in the form of polymeric deoxyribonucleotides. Anderson (1961) has described techniques for the isolation of nitrogenous bases from soil humic acids and applied his method to 12 samples of agricultural soil and one peat. The molar ratio of purines: pyrimidines varied from 0.35 to 0.92 indicating that some partly degraded DNA must be present. The total concentration of nitrogenous bases varied from 14 to 61 micromoles per 100 g of soil, accounting for an average of about 0.4% of the total nitrogen in the soil and 0.6% to 2.4% of the organic phosphorus in the soil. On the assumption that the soil nitrogenous bases are present in DNA-like materials, there should be one molecule of deoxyribose associated with each molecule of base. Thus, there should be 14 to 61 micromoles of deoxyribose per 100 g of soil in the form of DNA-like materials. In terms of humic acid, the total nitrogenous base content in one agricultural soil was 7.8 micromoles per g of humic acid (Anderson, 1958). Concentrations are such that they cannot totally be accounted for by presence in living microorganisms.

The nature of the organic matter of pre-Pleistocene soils has not apparently be enstudied.

Carbohydrates in Fossils

Although there was great discussion both before and after 1922 concerning the possible importance of cellulose in coal formation, it was not until that year that cellulose was isolated from material older than late Pleistocene. This was achieved by Gothan (1922) who discovered a natural pure cellulose, termed *sapperite,* in the Niederlausitz (Miocene) deposits of Germany. Its identity to cellulose was shown by microscopic examination (presence of woody fibers), and by colorimetric and solubility tests (Gothan, 1922; Wisbar, 1923, 1924). At about the same time, Schultz and Hamackova (1924) isolated cellulose from two Pliocene and two Miocene European lignites by alternate treatment with chlorine and sodium sulfite. That part of the residue which was soluble in Schweitzer's reagent (an ammoniacal solution of copper oxide used as a solvent for cellulose) contained 47.9% C and 6.2% H on a moisture- and ash-free basis (theoretical for cellulose, 44.4% C and 6.2% H). Sugars were produced on hydrolysis; one of the phenylosazone derivatives melted at 205°, the other at 208°. An attempt was made to prepare the octoacetate of cellobiose from the isolated cellulose. After several purifications the preparation melted at 226° (as compared to 228°–229° for authentic cellobiose octoacetate), but there was insufficient material left for further characterization. The two Pliocene samples contained 6.0 and 7.8% cellulose, and the two Miocene samples 0.2 and 11.4% cellulose on dry, ash-free basis.

At about the same time that the above work was developing in Germany, Komatsu and Ueda (1923) similarly analysed a Japanese fossil wood of unnamed age. The sample was found to contain 1.8% methylpentosans, 5.1% hemicelluloses, 29.4% cellulose, 56.2% lignin, and 1.03% ash. Cellulose was isolated by the method of Cross and Bevan, yielding a white powder with 44.0% C and 6.17% H on a dry, ash-free basis. D-Glucose was isolated after hydrolysis.

A sample of α-cellulose, originally isolated from a Miocene lignite by Opfermann and Rutz (1930), was later shown to have the same X-ray diffraction pattern as pure cellulose (Luft, 1930). This information, together with the chemical data mentioned above, left little doubt as to the validity of the identification of fossil cellulose.

It is historically interesting to note that Beyschlag (1938) considered the feasibility of manufacturing paper from lignitic cellulose. Staudinger and Jurisch (1939) investigated this possibility and discovered that the lignitic celluloses had a considerably lower degree of polymerization (DP) than did cotton and wood celluloses. Elemental analyses of several bleached lignitic pulps gave 44.4% C and 6.3% H in excellent agreement with the calculated values for cellulose, but a study of the specific viscosities of the fossil celluloses showed that the DP had fallen from an assumed initial value of 2000–3000 glucose units to 200–300 units in most preparations from Miocene samples. One exception had a DP of 750. These data showed that the cellulose molecule had been chopped into shorter units during geologic preservation. Other workers have since confirmed these findings. Reiff and Sohn (1943) and Reiff (1943) found DPs of from 40 to 800 in holocellulose preparations from various fossil lignites, mostly Miocene in age. Barghoorn (1948) and Barghoorn and Spackman (1950) similarly found low DPs in the holocellulose fractions isolated from early Tertiary lignites and fossil fruits. Cundy (1946) compared the loss of α-cellulose to the lowering of the DP of the α-cellulose in a Miocene *Sequoia* lignite, assuming no change in the lignin content of the wood during preservation. The change in DP was more marked than the loss of α-cellulose, showing that the cellulose molecules had been broken into a few relatively large fragments rather than many small ones. If many small fragments had been produced, little α-cellulose would have been left; most would have been converted to the shorter β- and γ-celluloses. It is important to note that celluloses obtained from archeological materials also have low degrees of polymerization. Celluloses prepared from Egyptian mummy wrappers were found to have DP values as low as 200 (Staudinger and Reinecke, 1939). Barghoorn (1949a) similarly reported that holocellulose fractions prepared from stakes of the Boylston St. Fishwier (about 4,500 years old) had much lower DP values than those from modern specimens of the same woods. It is not precisely clear as to when the major change in the DP occurs, but the available evidence suggests that it may be during the early stages of preservation.

Staudinger and Jurisch (1939) subjected dry cellulose to thermal degradation, both in the presence and absence of air, at temperatures ranging from 85 to 150°. Their data are given in Table 10. Inasmuch as many Miocene celluloses had been observed to have a DP of 200–300, these authors inferred that the temperatures during preservation must have been below 100–120°. Although there have been many studies of the thermal degradation of cellulose, few lend themselves to geologic application because the amount and nature of the cellulose remaining after a given treatment were not accurately measured. Berl (1940) found that the decomposition rates of cellulose heated in sealed containers varied with the charge density (grams of cellulose per milliliter volume of the container). Increasing the

TABLE 10.

Degree of Polymerization of Cotton Cellulose after Thermal Degradation (dry), both in Air and Vacuum

Initial DP = 2550. Data from Staudinger and Jurisch (1939)

Temperature (°C)	Time (days)	Degree of polymerization	
		Air	Vacuum
85°	4	2000	2150
105°	4	1200	2000
125°	4	190	1350
140°	4	150	830
150°	2	140	550
150°	4	140	350
150°	6	140	350

charge density from 0.02 to 0.2 g/ml increased the decomposition rate 16–20 times as measured by the production of gases. This was taken to be a pressure effect. The possible role of geologic pressures from rock overburden was thought to be similar. The older literature on the effects of heat on cellulose and some other carbohydrates was summarized by Hurd (1929).

A number of other workers have studied the preservation of cellulose and other carbohydrates in fossil woody materials. Miocene lignites containing as much as 37–45% holocellulose have been reported by Fuchs (1930), Schmidt, Tang and Jandbeur (1931), and Lieske and Winzer (1931). As might be suspected, local conditions are important in determining the degree of preservation of wood carbohydrates. Mahadevan (1933) analysed a lignite, a (bituminous?) coal, and an anthracite for cellulose. These were of identical age, but located in regions of differing tectonic histories. Cellulose was found in the lignite and coal, but not in the anthracite.

Local factors, even in a given deposit, may also be important in determining the degree of preservation. Staudinger and Jurisch (1939) found vertically adjacent lignites in which the cellulose content varied from 12 to 38% of the dry weight. Barghoorn (1949) has drawn attention to the fact that even within a given piece of lignite adjacent cells show varying degrees of cellulose preservation as revealed by microscopic examination. Varossieau and Breger (1951) and Varossieau (1953) studied 30–600 year old woods exposed by the bombing of Rotterdam during the war. Decomposition was shown to proceed from the outer surface inwards. Pentosans were found to disappear more slowly than cellulose.

The presence of lignin hinders decomposition of cellulose by microorganisms in the laboratory (Waksman and Cordon, 1938). Barghoorn and Spackman (1950) also noted that cellulose is best preserved in fossil parts that were originally rich in lignin.

Microbial decomposition of wood is hindered in water-rich environments. In the decomposition of wood in sub-aerial environments fungi are particularly active. Two processes may occur under these conditions: (a) "destruction" in which cellulose is destroyed with little attack on lignin; and (b) "corrosion" in which both lignin and cellulose are attacked (Waksman and Stevens, 1929). Studies on the microbial decomposition of cellulose have been reviewed by Waksman (1940). With regard to lignites and fossil woods, it seems to be generally agreed that decomposition is by chemical hydrolysis, rather than by bacterial and fungal attack (Mitchell and Ritter, 1934; Barghoorn, 1949a). The main evidence for this contention is: (a) fungal filaments are not observed in fossil woods and lignites; and (b) attempts to culture bacteria from wood stakes buried in marine muds gave negative results (Barghoorn, 1949a). Varossieau (1953), however, isolated bacteria from nearly all the buried wood that he examined.

On the assumption that no loss of lignin has occurred, one can calculate the amount of wood carbohydrates lost during preservation, provided that the lignite can be identified and a modern counterpart found for comparison. Mitchell and Ritter (1934) calculated that 70–75% of the original carbohydrates had been lost from some Miocene softwood lignites in California. In another Miocene deposit, Cundy (1946) calculated that 80% losses of pentosans and 80% losses of polyuronides had occurred as compared to 45% for cellulose, with an overall weight loss of 30–40% of the original *Sequoia* wood. Similar weight losses were given by Gortner (1938) for late Pliocene and early Pleistocene woods.

Jones and Merler (1956) briefly reported on the hemicelluloses of silicified wood of *Cedrus penhallowi* from a Miocene deposit. In addition to a cellulose-like fraction, a hemicellulose was extracted that yielded glucose, mannose, xylose, and glucuronic acid on hydrolysis. Brasch and Jones (1959), in a continuation of this work, isolated an *α*-cellulose fraction which yielded glucose and traces of mannose on hydrolysis. The α-cellulose formed 29.2% of the dry wood and had a DP of 95. A hemicellulose (extracted with 5% KOH from the wood) was also obtained. Attempts to fractionate the hemicellulose by solubility methods, precipitation, fractionation of derivatives and electrophoresis were unsuccessful. After partial hydrolysis the following were isolated as crystalline sugars or crystalline derivatives: D-glucose, galactose, D-mannose, L-arabinose, D-xylose, xylobiose, xylotriose and cellobiose. There was also chromatographic evidence of cellotriose, mannosido-glucose, 2-O-(4-O-methylglucuronosyl)-xylose, and 4-O-β-D-mannopyranosyl-D-glucose.

Brasch and Jones (1959) studied two additional lignites of interest, one from the McMurrary tar sands (lower Cretaceous) and the other from the Liblar mine near Cologne (lower Miocene). The tar sand lignite contained only 1.1% holocellulose (brown in color) that liberated D-glucose and mannose on hydrolysis in the ratio of 14:1. The Miocene lignite contained 3.2% holocellulose, and likewise yielded glucose and mannose on hydrolysis. A water-soluble fraction of the Miocene lignite, after repeated methylation, gave 2,3,6-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-glucose.

Little has been done on the remains of carbohydrates in fossils other than the work cited above on woody tissues. The presence of chitin in fossil marine invertebrates is often alluded to in geologic texts, however, close examination reveals that the statements are either based on pure assumption or else refer to C/N ratios in carbonaceous incrustations around arthropod fossils. There is one exception. Aberhalden and Heyns (1933) did isolate glucosamine from a hydrolysate of insect wing remains in a middle Eocene deposit. The specific rotation, $[\alpha]_D^{20}$ of the phenylhydantoin derivative was + 72.4° as compared to + 76° for the authentic compound. Drozdova and Kochenov (1960) have also found glucosamine in fossil fish bone.

Vinogradov and Boichenko (1943) applied color tests for pectins, hemicelluloses, cellulose and lignin to a series of living algae and higher plants, and to a limited number of fossil algae. It was noted that "primitive" algae (in general), and the fossil algae as well, were rich in pectins. These results indicate a profitable path for future study.

It is of theoretical interest to note that ABO blood group substances (carbohydrates) still remain in 5000 year old mummy tissues (Boyd and Boyd, 1937), and in bones of North American Indians.

Carbohydrates in Meteorites

It has been known for a century that certain types of meteorites, notably carbonaceous chondrites, contain organic substances in concentrations of a few per cent of the dry weight of the meteoritic matter. It has recently been suggested that this organic matter may have been formed by extraterrestrial biogenic processes (Nagy, Meinschein and Hennessy, 1961; Claus and Nagy, 1961). This raised the question of whether or not traces of unmodified biochemical constituents might be present in the meteorites. (see Chapter 1). The only investigators to pursue this problem so far are Egon T. Degens and his collaborators at the California Institute of Technology. They have reported the discovery of free amino acids and sugars (extractable with appropriate solvents at room temperature) and combined amino acids and sugars (solubilized only by acid hydrolysis) in several different carbonaceous chondrites (Degens and Bajor, 1962; Degens and collaborators, unpublished). Although reference to the results of amino acid analysis is beyond the scope of the present chapter, the data for carbohydrates are of direct interest. The concentrations of free sugars in several chondrites are given in Table 11 as recorded by Degens (unpublished). Five additional meteorite samples were analysed (Warrenton, Hvittis, Abee, Norton County (an achrondrite) and Bjurbole) in addition to those shown in Table 11, but no free sugars were detected in those cases.

Degens and Bajor (1962) found the total (free and combined) sugar concentrations to be 20 mg/kg and 70 mg/kg in air dried samples of the Bruderheim and Murray meteorites, respectively. In the former case the ratio of free to combined sugars was 1:1.5; and 1:2 in the latter. Paper chromatography revealed glucose with lesser quantities of mannose in both the free and combined fractions of each meteorite. A trace of arabinose was also found in the combined sugar fraction of the Murray. In interpreting these data together with the results of amino acid analyses the authors believed that contamination and/or extraterrestrial abiogenesis offered better explanations of the presence of these compounds in the meteorites than did synthesis by extra-terrestrial organisms.

Effects of Radiation on Carbohydrates

Geologically speaking, it is probably safe to assume that thermally-induced changes of sedimentary organic compounds are quantitatively more important than radiation-induced changes. However, given in sufficient dose, ionizing radiations do have a pronounced effect on organic compounds, and in some geologic situations the radiation effect may be important over long periods of time.

Literature on the radiation chemistry of organic compounds has been summarized by Collinson and Swallow (1956). At doses above 10^5 rep (roentgen equivalents physical) high-energy cathode rays act to depolymerize cellulose (Seaman *et al.*, 1952). A dose of 5×10^8 rep converted cellulose to water-soluble products. Destruction of the glucose in cellulose is measurable only at doses in excess of 10^6 rep (Seaman *et al.*, 1952; Charlesby, 1955). Ricketts and Rowe (1954) irradiated dextran with γ-rays from a Co^{60} source. A dose of 3×10^5 r resulted in a decrease of intrinsic viscosity; the viscosity decrease was more marked for an irradiated aqueous solution of dextran than for the irradiated solid.

TABLE 11

Quantities of Free Sugars in Various Chondrites (data from Egon T. Degens and co-workers, unpublished). The Classification of Chondrites is that given by Wiik (1956). *Concentrations are given as mg of free sugar per kg of air dry meteorite. See text for other data.*

Meteorite	Glucose	Mannose	Arabinose	Xylose	Total
Carbonaceous chondrites:					
Type I					
Orgueil	3	5	tr	—	8
Type II					
Cold Bokevelt	—	tr	—	—	tr
Meghei	tr	tr	—	—	tr
Murray	6	17	1	—	24
Type III					
Felix	—	tr	—	—	tr
Mokoia	2	2	1	—	5
Enstatite chondrites:					
Hvittis	9	14	—	3	26

Wolfrom (1957) has studied the action of ionizing radiations on a variety of carbohydrates. High velocity electrons in doses of $>10^6$ rep were found to hydrolyse poly- and oligosaccharides to their component sugars. Gamma-irradiation ($4 \times 10^6 \nu r$) converted mannitol to mannose and aribinose. At higher doses some mannuronic acid was produced. Lawton *et al.* (1951) subjected basswood to irradiation with high-energy electrons. Below 5×10^6 rep, there was no weight loss, acid production, or change in pentose, reducing, and phenolic groups; above this value, detectable changes occurred.

Barker *et al.* (1959) found that sugar monomers in aqueous solution tended in part to polymerize when irradiated with a Co^{60} source. The polymerization manifested itself only in the absence of oxygen. Thus, irradiation of 0.1% glucose solutions in the presence of oxygen yielded gluconic acid predominantly and no polymer, whereas in the absence of oxygen the following compounds were detected: polymers, glyoxylic acid, tartaric acid, oxalic acid, formic acid and CO_2. Irradiation of oxygen-free maltose solutions resulted in the formation of polymers, glucose, gluconic acid, maltobionic acid and other compounds.

Interaction of Carbohydrates with Clays

Addition of microbial gums to soil brings about an aggregating effect that may change the physical texture to favor plant growth (Martin, 1945, 1946; Rennie *et al.*, 1957). Chesters *et al.* (1957) recently subjected soil data to multiple regression analysis. Microbial gum (measured by a modified Forsyth technique—see the section on soils) was found to be the most important factor in aggregation, except when iron and clay contents were high, at which time each of the latter exerted an important influence. Total organic matter showed only a slight statistical importance, indicating that the effect of the organic matter was caused by its microbial gum content.

Although the exact manner of occurrence of carbohydrates in soil has yet to be elucidated, it seems reasonable from laboratory data that some carbohydrates may be associated with clay minerals. Lynch *et al.* (1956) have shown that polysaccharides are strongly sorbed on montmorillonite (0.02–120 mg carbohydrate per gram of clay at saturation, the value depending on the carbohydrate), though much less so on kaolinite (0–3.7 mg carbohydrate per gram of clay at saturation, for the same series of carbohydrates). The C-axis of the montmorillonite crystal is expanded when polysaccharide-clay complexes are formed (Lynch *et al.*, 1956); this is also true for complexes with sugars and sugar derivatives (Greenland, 1956a, 1956b). Hydrogen-bonding is apparently the important factor in holding non-acidic carbohydrates in the clay lattice, whereas acidic carbohydrates, such as pectic and alginic acids, appear to be held on anion-exchange sites (Lynch *et al.*, 1957). Montmorillonite binds polysaccharides more than oligosaccharides, and these in turn more than monosaccharides. Sorption does not progressively increase with increasing molecular weight; cellulose dextrins are more effectively sorbed than either shorter or longer polymers. The sorption of carbohydrate phosphates on bentonite, illite, and kaolinite has been studied by Goring and Bartholomew (1951); bentonite exhibited the greatest sorption.

Lynch and Cotnoir (1956) showed that the polysaccharides in polysaccharide–montmorillonite complexes are not decomposed so quickly by soil microorganisms and enzyme preparations as are the same free polysaccharides. Under comparable conditions the complexes with illite and kaolinite afforded little or no protection. Attapulgite (intermediate in crystal structure between montmorillonite and kaolinite) behaves like montmorillonite in this respect (Lynch *et al.*, 1957). Decomposition was measured over periods of a few weeks in the above experiments. Whether the interlattice stability of polysaccharides can persist over several years or more is a moot question (Lynch and Cotnoir, 1956). In any case, decomposition does occur in interlattice sites, but at relatively slower rates.

Interaction of Carbohydrates and Amino Compounds

Fifty years ago Maillard (1911) drew attention to the fact that amino groups of amino acids interact with the reducing groups of aldoses and ketoses to form, after a complex series of reactions, a mixture of brown polymers termed melanoidins. The reaction, which has subsequently come to be known as the Maillard or browning reaction, proceeds in two stages: the formation of glycosylamines or N-substituted glycosylamines, followed by a complex series of events eventually leading to the formation of brown polymers. The best recent review of the subject is given by Ellis (1959). It is of interest to note that the reaction can occur between basic amino acids and sugars even when the former are present in polypeptides (Patton, Hill and Foreman, 1948). Lysine is typically the most reactive of all amino acids. Among sugars the series in order of increasing reactivity is: dissaccharides, hexoses, pentoses. Some monosaccharide decomposition products are highly reactive.

Geochemical interest in the Maillard reaction arises from the following facts: (a) the reaction proceeds readily in the temperature range of 20°C to 140°C depending on the reactivities of the compounds involved and their concentrations; (b) it occurs under both aerobic and anaerobic conditions; and (c) the pH and water concentrations most favorable for the reaction (pH 7–10; 0.1–90% water) encompass the values characteristic of most sediments. Drozdova (1957, 1959, and earlier work) has stressed the probable geochemical importance of melanoidin-forming reactions particularly in relation to chitin transformation. Kononova (1961) suggests that some formation of non-aromatic humic acids in soil may occur via the Maillard reaction. On the other hand, if the reaction were important in nature one would certainly expect to find some evidence of it in sediment cores, particularly in terms of the ratio of basic to non-basic amino acids in sedimentary polypeptides as a function of depth; however, an examination of published data fails to show any marked selective decomposition of basic amino acids in buried sediments. Also, the percentage of lysine in the total amino acid shows no characteristic decline with increasing depth: the percentages are about the same as those characteristic of living microorganisms.

Carbohydrates in Relation to Inorganic Elements

It is beyond the scope of the present chapter to go into detail on this point, but it is worthy of note that carbohydrates do form compounds with sulfates, phosphates, and ammonia, and complexes with borate. Acidic carbohydrates, such as alginic acid and pectic acid, normally occur as calcium and magnesium salts. There is also some evidence that cellulose and other carbohydrates may form silicon complexes (Viehoever and Prusky, 1938; Holzapfel, 1951; Engel, 1953), but whether the complexes are physical or chemical remains to be demonstrated.

Concluding Remarks

Although the geochemistry of carbohydrates has been studied in considerable detail, the subject is still in its infancy.

A number of factors may influence the decomposition of carbohydrates and other organic compounds under geologic conditions. Decomposition by micro-organisms is particularly important on the earth's surface, but it is greatly reduced after burial in wet muds. Depending on the particular environment of preservation, such factors as presence of other organic compounds, pressure, ionizing radiations, oxidation, catalysis, and solution processes may be important. Differential destruction of dissimilar carbohydrates under a given set of conditions is to be expected. It is clear from the work that has already been done on soils and sediments that fructans are particularly labile.

It is difficult to predict the future importance of carbohydrates in geochemical considerations. Reference has been made to the possible ecological role of carbohydrates in affecting the physiological behaviour of oysters. Microbial gums are important in determining soil texture thus affecting plant growth and soil erosional processes. Other ecological roles for carbohydrates remain to be learned.

The possible use of fossil carbohydrates as low-temperature geothermometers seems promising, but more detailed laboratory data must be accumulated before reliable interpretations can be made. One of the most pressing needs is for data concerning the transformations of carbohydrates (more generally, all organic substances) at two conceptual interfaces: (a) living organism–dead organism; and (b) unconsolidated sediment–sedimentary rock. From present data, one must infer marked destruction at these boundaries, but whether this is really so remains to be determined.

Carbohydrates are present in bone (Stack, 1955; Eastoe, 1956) and teeth (Stack, 1954, 1955), but no one seems to have examined fossil bones and teeth for them. The relative stabilities of proteins and polysaccharides in these materials would make an interesting study in itself.

From time to time various workers have suggested that carbohydrates play a dominant role in the formation of coal and petroleum. The possible role of carbohydrates in coal genesis is discussed elsewhere in this book; little can be said with regard to petroleum formation from carbohydrates. Berl (1940) and others have shown that the pyrolysis of carbohydrates in the laboratory leads to the formation of petroleum-like fractions. Whether there is a geologic counterpart to this process is a moot question. When more is known of the nature and abundance of carbohydrates in sediments and sedimentary rocks, it may be possible to give a concrete answer to this and other questions.

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CHAPTER 12

GEOCHEMISTRY OF LIPIDS*

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Introduction

This chapter is concerned with lipids, their occurrence, their structures and their geochemistry. Admittedly, "lipids" is a term which is used confusedly and interchangeably to designate many kinds of substances that are "fatty" in appearance and not only for "fats" as chemically defined. In this review the term "lipids" will embrace all organism-produced substances that are soluble in water with difficulty but are extractable by one or another of the so-called fat solvents such as chloroform, carbon tetrachloride, ethers, aliphatic and aromatic hydrocarbons, and acetone. Of primary importance among such substances are the groups of compounds which Bloor (1926) called "simple lipids". These are the true, neutral fats, which are the fatty acid esters of glycerol, and the true waxes, the fatty acid esters of higher aliphatic alcohols. As used in this chapter, the term "lipids" also includes Bloor's "derived lipids", which comprise free aliphatic fatty acids, alcohols and hydrocarbons, and branched acyclic or cyclic compounds belonging to the groups of terpenoids and steroids.

A biochemical definition of lipids, no matter how comprehensive, must restrict the term to compounds that are or have been produced by organisms. Substances such as mineral oil are excluded. The discussion of the geochemistry and fossil occurrence of lipids is restricted to compounds that can either be directly related to past or present products of life's activity, or which possess a structure that leaves little doubt as to their relationship to such products. Thus, in dealing with fossil fuels derived from accumulations of former life's products, only those few known compounds that are identical with or closely related to recent lipids will be considered.

In addition to a discussion of individual recent and fossil lipids, certain geochemical aspects of lipids will be considered. The geochemical history of neutral fats, albeit quite fragmentary, will be dealt with separately, as will be the much better documented history of the waxes. Because algae and diatoms have been regarded as certain or probable sources of particular

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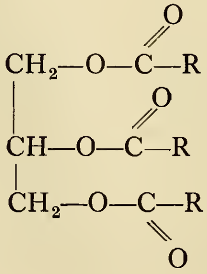
fossil fuels, special treatment has been given to the occurrence and chemical nature of their lipids, and to the circumstances under which they might accumulate and be transformed. A parallel discussion considers marine animals with special emphasis on the lipids of reef-building organisms and other marine invertebrates.

Acyclic Compounds

Introduction—When organic chemists first became acquainted with the saturated, straight-chain hydrocarbons, $CH_3(CH_2)_nCH_3$, they were sufficiently impressed by their inertness and lack of chemical activity to name them paraffins, a word derived from *parum affinis*, meaning "of slight activity". Since then it has been shown that these paraffins are not quite as inert as originally believed, and that they may be oxidized, halogenated and nitrated under special laboratory conditions. Nevertheless, hydrocarbons remain most prominent among the organic compounds that show the greatest resistance to the destructive forces of the elements such as the chemical action of inorganic compounds, the oxidation by air, or the solvent power of water. Relative inertness is also demonstrated by acids, $CH_3(CH_2)_nCOOH$, and alcohols, $CH_3(CH_2)_nCH_2OH$, in which the CH_2–chain is of sufficient length to confer upon such compounds greatly reduced volatility and solubility in water. It is because of their great inertness that the higher paraffins, fatty acids and alcohols belong to the most stable compounds common in animal and plant tissues and, consequently, to those most likely to accumulate on the death and decay of the system that produced them.

Compounds with long, unbranched chains of CH_2-groups are the most conspicuous components of the lipid or fatty fractions of animals and plants. With but few exceptions, such as the phosphatides, these lipids are only slightly soluble in water, but very soluble in ether, benzene, chloroform, and carbon tetrachloride. From a quantitative point of view, the most important lipids are the true fats or triglycerides, and the waxes. Although the former represents a rather well-defined group of compounds of the general structure I, the latter may embrace several groups of compounds, such as esters, alcohols, ketones and hydrocarbons.

Triglycerides—In the common triglycerides (I) R may represent a saturated group



I

such as the n-pentadecyl (— $(CH_2)_{14}CH_3$), or heptadecyl (—$(CH_2)_{16}CH_3$) group of palmitic ($C_{16}H_{32}O_2$), or stearic ($C_{18}H_{36}O_2$) acid, or unsaturated groups such as —$(CH_2)_7CH{=}CH(CH_2)_7CH_3$ or

$$—(CH_2)_7CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH_3$$

of oleic and linoleic acid. An abundance of saturated R-groups results in a solid fat; increasing unsaturation leads to an oil. The more unsaturated the R-group, the more subject it will be to the destructive action of chemical agents such as atmospheric oxygen. In a hydrating, mildly oxidizing or reducing medium, the unsaturated units may be converted into relatively more stable hydroxy derivatives or the rather inert saturated groupings.

Treatment of glycerides with alkali leads to neutral, water-soluble glycerol and the "soaps", which are easily converted into the free fatty acids by treatment with mineral acids. The most common of the fatty acids are those containing sixteen and eighteen carbon atoms. As a rule, the saturated acids predominate among acids having a chain-length of sixteen carbon atoms or less; among them palmitic acid is the most common of all saturated acids. The situation is reversed among the acids containing eighteen or more carbon atoms. Here the unsaturated acids are the more conspicuous, and oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, is not only the most common of the C_{18}-acids but the most ubiquitous of all the fatty acids. Among the acids participating in the formation of triglycerides an increasing chain length is generally accompanied by an increasing degree of unsaturation. Highly unsaturated and rather unstable acids of the order C_{20}, C_{22} and C_{24} are quite common in the triglyceride oils of marine fishes and other marine animals.

Waxes—A true triglyceride, when treated with alkali, is converted completely into water-soluble substances, glycerol, and soaps. Under similar conditions a wax is only partly solubilized. A considerable fraction, the unsaponifiable matter, remains dispersed in or floats on the soap solution from which it may be separated by means of solvents such as ether. Acidification of the soap solution yields fatty acids, mainly of the straight-chain type. The unsaponifiable fraction is often a complex mixture composed of straight-chain alcohols, hydrocarbons and ketones, and of branched, acylic or cyclic terpenoid compounds which will be dealt with elsewhere.

A typical wax is the ester of a higher aliphatic acid and a higher aliphatic alcohol. An example is cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$, a common constituent of lower marine invertebrates and the principal component of *spermaceti* from the head of the sperm whale. When treated with sodium hydroxide it affords the water-soluble sodium palmitate and the unsaponifiable, ether-soluble cetyl alcohol. Esters of considerably higher molecular weight mixed with higher hydrocarbons are the principal components of the plant waxes which coat the leaves, the needles, and the fruits of most plants thereby offering them the protection of their impermeability and chemical inactivity. Waxes may occur in quantities sufficiently large to warrant their commercial exploitation, such as the Carnauba wax of certain Brazilian palm leaves, or be present only in thin but significant layers which give the leaves their sheen and the apple its polish. Waxes of similar composition also cover the cuticles of the exo-skeletons of insects.

As already noted, the acid moieties of largest molecular weight in the triglycerides are generally the most unsaturated. In waxes destined to afford surface protection such unsaturation would be most undesirable and it is, therefore, not surprising that the acids and the other wax components are mainly, if not entirely, saturated. The isolation and subsequent identification of individual components of a typical wax mixture are fraught with difficulties. Chibnall and his associates (see Piper *et al.*, 1934) deserve credit for having brought order to a chaotic situation two decades ago by introducing modern techniques for the characterization and identification of long-chain compounds, whether they are the acids of the saponifiable fraction, or the alcohols, hydrocarbons, or ketones of the unsaponifiable moiety of waxes. These authors have shown in numerous papers that the acids and alcohols are of the order C_{22}–C_{32} with an even number of carbon atoms arranged in a straight chain, and that in contrast the paraffinic hydrocarbons are of the order C_{25}–C_{35} with an odd number of carbon atoms. Biochemically, the fatty acids are synthesized from two-carbon units, and hence the final products possess an even number of carbon atoms. The higher alcohols may be viewed as being formed by reduction of the carboxyl group with retention of the same number of carbon atoms. The hydrocarbons, however, are products of acid decarboxylation which, whatever the mechanism, must lead to the formation of odd numbered hydrocarbons.

Fossil fatty acids. There exist a number of reports on the fossil occurrence of fatty acids, of lower or medium molecular weight, which may safely be regarded as former components of triglycerides or waxes, or as fragments of such components.

Various fatty acids have been isolated from petroleum. Tanaka and Kuwata (1928) obtained a small fraction from an Ishikari petroleum distillate which consisted of 20% myristic ($C_{14}H_{28}O_2$), 45% palmitic ($C_{16}H_{32}O_2$), and 20% stearic ($C_{18}H_{36}O_2$) acid. They found the same acids in similar proportions in other petroleums from Japan, California and Borneo. In addition to the acids found by the Japanese investigators, Lochte (1952) observed arachidic acid ($C_{20}H_{40}O_2$) in the gas oil from Japanese and Polish crude oil. Arachidic acid had previously been found in Boryslaw petroleum by Holzmann and von Pilat (1931). Tanaka and Kuwata (1928) called attention to the fact that the saturated fatty acids found in petroleum are also the principal solid acids of the fats and waxes of sharks and whales. They have suggested that the lipids of these fish and mammals, which were so abundant in the Mesozoic and Tertiary periods, may well have been a principal source of petroleum.

Schreiner and Shorey (1908), pioneers in the organic chemistry of soils, found dihydroxystearic acid, $CH_3(CH_2)_7CHOHCHOH(CH_2)_7COOH$, in soils of low fertility. Its concentration was fifty parts per million or 200 lb/acre-ft. It was suggested that this acid, viewed as an oxidation product of oleic acid, is toxic and in part responsible for the poor fertility of the soil. Fatty acids of the order C_{26}–C_{30} have been isolated by Trask and Wu (1930) from recent marine sediments where they occur in concentrations from 20–60 p.p.m. The investigators considered it quite likely that additional amounts of acids had been present as calcium or magnesium salts, and had thus resisted extraction with carbon tetrachloride. Schreiner and Shorey (1910) isolated α-hydroxystearic acid, $CH_3(CH_2)_{15}CHOH$-$COOH$, from the Elkton silt loam of Maryland, and lignoceric acid from a peaty soil. Magnesium and calcium salts of oleic acid have been obtained from a Black Sea ooze (Shabarova, 1954), and fatty acids of high molecular weight have been found in the waters of Beloe Lake in Russia (Goryunova, 1954).

Fatty acids of relatively low molecular weight, often of uncertain origin, have also been found. Stadnikov and Kashtanov (1929), by extracting Russian boghead coal with benzene, obtained fatty acids of an average molecular weight of $C_{12}H_{24}O_2$. Subsequent extraction of the coal with 5% sodium hydroxide followed by acidification gave caproic acid, $C_6H_{12}O_2$, enanthic acid, $C_7H_{14}O_2$, and caprylic acid, $C_8H_{16}O_2$. The authors believed these acids to be the fragments of a polymer formed originally from the unsaturated fatty acids in the source material of the boghead coal. The isoamylacetic acid and diethylpropionic acid which Chichibabin *et al.* (1932) isolated from petroleum from Baku are probably fragments of terpenoids rather than related to the normal fats or waxes. Caproic acid, $C_6H_{12}O_2$, has been isolated from a limestone-forming sediment from Florida Bay (Trask and Wu, 1930), and valeric acid has been found in a Black Sea mud (Shabarova, 1954). The latter acid is more likely the product of protein rather than lipid degradation.

Hydrocarbons—Paraffinic, straight-chain hydrocarbons are probably present in all non-saponifiable fractions of natural fats, oils and waxes. From the chemists' point of view they are rather uninteresting compounds. Only in comparatively rare instances have special efforts been made to look for, isolate, and study them. In most cases their presence is noted only in passing, mainly because they happened to separate as a crystalline fraction. These hydrocarbons are usually identified by melting points and carbon–hydrogen analyses. Such criteria are quite inadequate properly to identify the solid paraffins. Melting points are subject to considerable variations caused by impurities, and the carbon–hydrogen ratios are so similar in homologous higher hydrocarbons as to make their differentiation by this technique difficult if not impossible. (cf. $C_{25}H_{52}$: C, 85.14%; H, 14.86%; $C_{26}H_{54}$: C, 85.16%; H, 14.84%). As in the case of the higher acids and alcohols, it was Chibnall and his associates who applied new criteria, such as the polymorphic behavior, for the identification of solid hydrocarbons, and who introduced with conspicuous success the technique of X-ray diffraction measurements. By means of these new methods it was shown by 1940 (Smith, 1939) that only a few of the solid, natural hydrocarbons then known could be regarded as reasonably pure, and that most were mixtures of homologues. All naturally occurring straight-chain paraffins then investigated were found to contain an odd number of carbon atoms, and the suggestion was made that all hydrocarbons of this group were similar. This rule has been found so satisfactory that any hydrocarbon seeming to deviate from it must be viewed with suspicion until its structure has been established beyond reasonable doubt.

Although hydrocarbon-like material has been extracted from many sediments (see for example Smith, 1954), in only a few instances have hydrocarbons been isolated which with reasonable assurance may be viewed as being identical to hydrocarbons obtained from living matter. The earliest observation relative to them was made by Schreiner and Shorey (1911b) who isolated from a peaty North Carolina soil a hydrocarbon which melted at 68° and which they believed to be $C_{31}H_{64}$. Petrova *et al.* (1956) recently isolated a solid hydrocarbon melting at 52° from a Russian clayey silt which was low in bituminous material. This compound represented 18.7% of the total hydrocarbon present. Another sediment, richer in bitumen, also yielded a solid hydrocarbon melting at 59.5°. These melting points are well within the range of the hydrocarbons, $C_{25}H_{52}$, $C_{27}H_{56}$ and $C_{29}H_{60}$, and they may indeed represent original material.

Comparatively little is known about the distribution in nature of paraffinic hydrocarbons belonging to the intermediate group between $C_{15}H_{32}$ and $C_{25}H_{52}$, or to the lower group containing fifteen carbon atoms or less. Hydrocarbons of the intermediate group have not previously appealed to the chemists because of their often Vaseline-like consistency, and by the difficulties of their purification by either crystallization or distillation. The only hydrocarbon from this group whose natural occurrence has been ascertained beyond doubt is heptadecane, m.p. 22.5°, a component of sardine oil (Toyama, 1935).

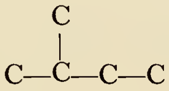
Members of the lower group if present, may well be overlooked unless they occur in considerable quantities or unless special efforts are made to search for them. In many studies on the isolation and composition of the unsaponifiable matter of animals and plants no special precautions have been taken to prevent the loss of smaller amounts of lower boiling hydrocarbons through evaporation during preparation for analysis. Until quite recently such hydrocarbons were known only in oils conspicuously rich in them. It may be assumed, however, that they enjoy a much wider distribution than is known at present, and that their more frequent occurrence will be revealed through the application of new techniques such as vapor phase chromatography and mass spectroscopy. The rule of the uneven number of carbon atoms also applied to the lower members of the series.

In his book, *The Non-Benzenoid Hydrocarbons*, Brooks (1922) could still state that "n-heptane enjoys the distinction of being the only hydrocarbon other than the solid paraffins formed by phytochemical processes". It is this component which gives the petroleum nuts of the Phillipines their easy flammability, and is also present in the oils of many species of pines, such as the Jeffrey pine oil, which contains 98% of n-heptane.

In recent years n-nonane has been found in pine oil (Rock, 1951). This hydrocarbon had first been discovered in the volatile oil of *Sarothra gentianoides* (Bogert and Marion, 1933), and later was shown to constitute 60% of the essential oil of the New Zealand tree, *Pittosporum eugenioides* (Carter and Heazlewood, 1949). Undecane, $C_{11}H_{24}$, is also present in pine oils, such as the one obtained from the ponderosa pine (Iloff and Mirov, 1954), and from other species (Rock, 1951). It is of interest that undecane is the principal constituent of the volatile oil obtainable from ants such as *Formica rufa* (Schall, 1892). As yet tridecane does not seem to have been found in living material, but pentadecane, $C_{15}H_{32}$, has been claimed to be a component of Sanna-oil (Nakao and Shibuye, 1924).

Terpenoids

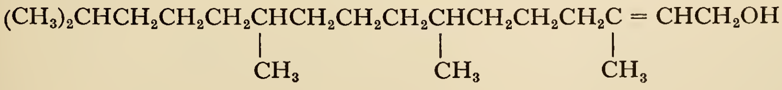
Definition—A very large number of naturally occurring compounds of bewildering diversity may be viewed as being constructed from branched five carbon isoprene units.



$$\mathrm{C{-}\overset{\overset{C}{|}}{C}{-}C{-}C}$$

Compounds based on such units are called terpenoids. They may conveniently be divided into the monoterpenoids, containing two isoprene units, the sesquiterpenoids, C_{15}, the diterpenoids with four isoprene units, C_{20}, the triterpenoids, C_{30}, consisting of six isoprene units, and the polyterpenoids containing even more such units. The various types may occur either in a linear arrangement of their units or cyclized into as many as five or more ring systems (see Simonsen and Owen, 1947–1957).

Acyclic compounds—Among the linear monoterpenoids and sesquiterpenoids are many of the pleasant smelling hydrocarbons, alcohols, aldehydes, and ketones, important components of the essential oils of many plants. All have relatively high vapor pressures and evaporate relatively rapidly unless accumulated and preserved under unusual circumstances. The most widely distributed acyclic diterpenoid is

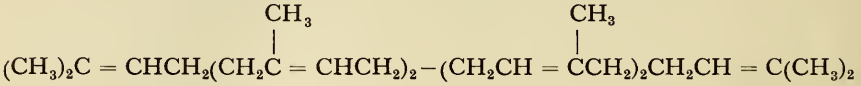


$$\mathrm{(CH_3)_2CHCH_2CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_2\underset{\underset{CH_3}{|}}{C}=CHCH_2OH}$$

II

phytol (II), a moiety of the chlorophyll molecule. This ubiquitous substance of the plant world is constantly being produced in amounts of staggering magnitude. Little is known, however, about the destruction of chlorophyll after the death of the cell, or of the fate of its isoprenoid component, the phytol. Because of its structure, we may expect phytol to be comparatively stable, and hence to be found as such or in a modified form in subfossil or even fossil material.

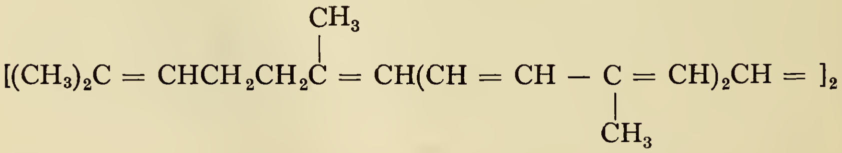
A triterpenoid hydrocarbon which is widely distributed in the animal world is squalene (III), whose great biochemical significance is only now being fully appreciated. It is found in many animals and plants and particularly in shark-liver oil, from which it may be obtained in substantial quantities. Because of its hydrocarbon nature and its occasional abundance in fish, it has been included among those naturally occurring compounds which might have contributed to the formation of petroleum (Ormandy *et al.*, 1927).



$$(CH_3)_2C=CHCH_2(CH_2\overset{\displaystyle CH_3 \atop |}{C}=CHCH_2)_2-(CH_2CH=\overset{\displaystyle CH_3 \atop |}{C}CH_2)_2CH_2CH=C(CH_3)_2$$

III

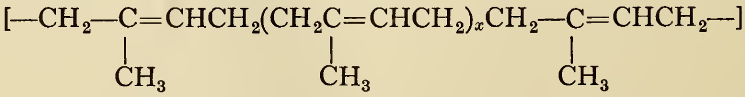
Eight isoprene units arranged linearly, or with but one or two single rings at the ends of the chain, are present in the very common natural red or yellow pigments, the carotenoids, among which lycopene (IV) is one of the simplest representatives. Because of their unsaturation they have but a transitory existence in the presence of light and air. Suitably protected, however, they may survive for a considerable length of time as evidenced by their presence in comparatively recent sediments (see Chapter 9) (Andersen and Gundersen, 1955; Fox, 1944).



$$[(CH_3)_2C=CHCH_2CH_2\overset{\displaystyle CH_3 \atop |}{C}=CH(CH=CH-\underset{| \atop \displaystyle CH_3}{C}=CH)_2CH=]_2$$

IV

The longest chains, composed of many isoprene units, are encountered in the natural rubbers such as caoutchouc (V) and gutta-percha. The so-called mineral

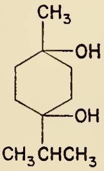


$$[-CH_2-\underset{| \atop \displaystyle CH_3}{C}=CHCH_2(CH_2\underset{| \atop \displaystyle CH_3}{C}=CHCH_2)_xCH_2-\underset{| \atop \displaystyle CH_3}{C}=CHCH_2-]$$

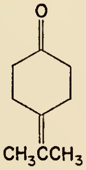
V

caoutchouc, elaterite, is not a true rubber in the chemical sense. The fossil occurrence of true rubber, however, has been convincingly demonstrated. The "monkey hair", a soft, fibrous and elastic material which is occasionally found in form of balls in certain German lignites, has been shown by Kindscher (1924) to be almost indistinguishable from fresh natural rubber. His observations have been verified and supplemented by others. Gothan (1927) and Jurasky (1928) have shown that, like natural rubber, the fossil material may be ozonized to a true ozonide which upon decomposition affords the typical levulinic aldehyde, and also that it may be vulcanized in the normal manner. It is probable that some of the resinous material found in hard coal may be modified rubber (Eck, 1930). While it is not inconceivable that the fossil rubber may be the product of a slow polymerization of other isoprenoid material, it appears more likely that it has been derived from latex bearing trees.

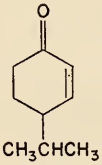
Cyclic compounds—The most diverse of the terpenoids are those with cyclic structures. The variety of ring systems seems limited only by the number of isoprene units involved and the head-to-tail attachment of the units. Many of the cyclic monoterpenes may be regarded as derivatives of cyclohexane, and most of them may be readily converted into derivatives of benzene by simple dehydrogenation procedures. In spite of their relatively high volatility, cyclic monoterpenoids have been found in subfossil, if not fossil formations. One of the best-known examples is the occurrence of terpene hydrate, $C_{10}H_{20}O_2 \cdot H_2O$ (VI), in the fossil woods of the San Francisco Mts., north of Flagstaff, Arizona, which are believed to be more than 500 years old. This material was first described by Guild (1922) under the name of Flagstaffite.



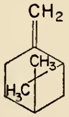
VI



VII



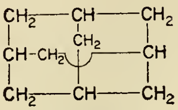
VIII



IX

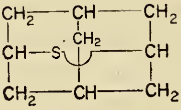
4-isoPropylidenecyclohexanone (VII) has been isolated from lignite resins by Ruhemann and Rand (1932). This compound, and its isomer (VIII), had previously been known as constituents of pine needle oil and eucalyptus oil. Although they are not terpenoids in the true sense of the word, they may easily be derived from β-pinene (IX), a component of many aromatic plant oils.

A compound with an empirical structure, $C_{10}H_{16}$, reminiscent of that of monoterpenes, is adamantane (X). This extraordinary compound has been isolated from higher boiling petroleum fractions (Landa and Machaček, 1935). Adamantane, which has a camphoraceous odor, is one of the most symmetrical of all the organic compounds and melts at 263°. The graphic representation (X) does not do justice to the beauty and symmetry of its three-dimensional structure. Its structural relationship to known terpenes is uncertain. Replacement of one of the CH_2-groups of adamantane by sulfur leads to thia-adamantane (XI), a compound which has been found in Middle East Oil distillates (Birch *et al.*, 1952).



Adamantane

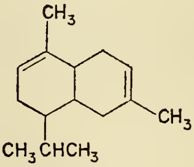
X



Thia-adamantane

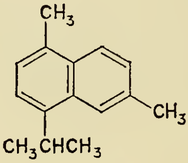
XI

Many cyclic sesquiterpenes may be viewed as derivatives of decalin and many of them may indeed be converted into naphthalene derivatives. Examples are the widely distributed cadinene (XII) into cadalene (XIII). It is probable that the 1,2,5-, 1,2,7- and 2,3,6-trimethylnaphthalenes which Carruthers and Douglas (1955) isolated from Trinidad crude oil have been derived from sesquiterpenes (see Chapter 7 and Robinzon and Grishina, 1956).



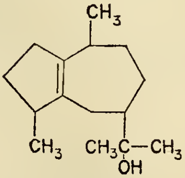
Cadinene

XII



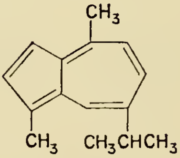
Cadalene

XIII



Guajol

XIV

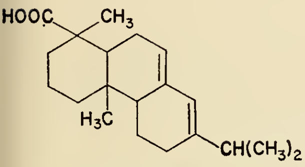


Azulene

XV

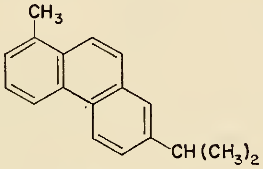
It has been known for a long time that higher boiling fractions of many essential oils contain blue hydrocarbons, the azulenes. Their structural relation to a number of sesquiterpenes has recently been demonstrated. Thus the sesquiterpenoid alcohol guajol (XIV), a component of the wood oil from Australian pines, upon heating with sulfur yields the blue 1,4-dimethyl-7-isopropylazulene (XV). Such azulenes have recently been found in the fossil resins of the lignite deposits from Warkalay, India (Varier, 1950).

With increasing molecular weight the vapor pressure of a terpenoid is reduced and the chances of its fossil occurrence are increased. The most common diterpenoids are the resin acids, components of pine rosin; among them abietic acid (XVI) is the most ubiquitous. This acid has been found in bituminous coal (Golumbic *et al.*, 1950). Abietic acid is very readily dehydrogenated to retene (XVII), an aromatic hydrocarbon often found in fossil pine wood. Fichtelite (XVIII), a non-aromatic hydrocarbon even more closely related to abietic acid, has also been found in many fossil woods. Other related compounds that are found in lignites in the form of white crystals have been described under a variety of names, such as hartite, hofmannite, branchite and bombiccite (Soltys, 1929). They are probably all identical with iosene, m.p. 74°, a hydrocarbon, present to the extent of 1% in a certain Austrian (Piberstein) lignite (Soltys, 1929). Iosene (XIX) is identical with α-dihydrophyllocladine, m.p. 74.5°, $[\alpha]_D = 23.9^\circ$ (Briggs, 1937), a constituent of essential oils which yields retene upon dehydrogenation (Brandt, 1952).



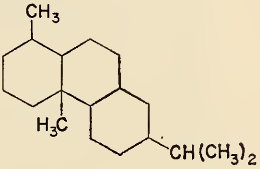
Abietic acid

XVI



Retene

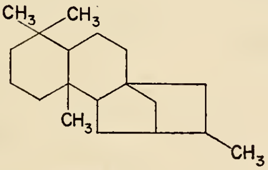
XVII



Fichtelite

XVIII

Related compounds are also found in the fossil resins of commerce such as copals that are formed when various natural rosins decay and become fossilized under anaerobic conditions. Many fossil resins have been examined, and the majority have been found to contain retene (XVII) and fichtelite (XVIII) (Sterling and Bogert, 1939), and in some cases also agathenedicarboxylic acid (XX) (Ruzicka and Hosking, 1929).

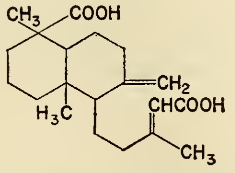


Iosene

XIX

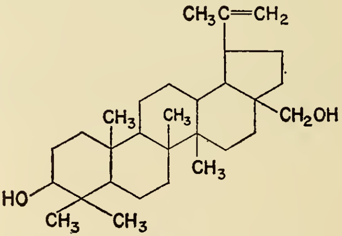
Triterpenoids—Widely distributed in the world of higher plants are the triterpenoids. These polycyclic compounds containing thirty carbon atoms possess a rather complex structure which has only been elucidated in recent years. A common representative of this group is betulin (XXI), which may be present to the astonishing extent of 35% in the outer bark of white birches. Betulin, and its derivatives, allobetulin and oxyallobetulin, have been isolated by Ruhemann and Rand (1932) in significant quantities from the resinous fractions of the extractable, bituminous material of German lignites. These authors refer to the compounds as sterols in disagreement with the more modern definition which restricts the term "sterol" to those compounds discussed below. A compound melting at 237°, and which is probably related to betulin, was isolated from the Marshall clay of North Dakota by the pioneers of organic geochemistry (Schreiner and Shorey, 1909). This soil, which has an organic content of 10.6%, contains 250–300 ppm of this crystalline material which the authors named agrosterol. They calculated that it was present to the extent of 1000–1500 lb/acre-ft. Of similar nature appear to be the compounds, m.p. 244–247°, isolated by Zechmeister and Frehden (1939) from lignite, and by Pschorr and Pfaff (1920), m.p. 241°, from montan wax. The fraction of montan wax which is soluble in hot isopropanol has recently yielded a complex mixture of triterpenoids from which the following have so far been isolated: friedelin, friedelan-3β-ol, oxyallobetulone, and oxyallobetulin (Jarolim *et al.*, 1958).

Dimethylpicene (XXII), a substance most certainly derived by dehydrogenation of a triterpenoid, has been found in the Japanese Yubari coal (Sakabe and Sassa, 1952). Even more remarkable, and of far-reaching importance, is the occurrence of oxyallobetul-2-ene (XXIII) in some of the higher boiling fractions of petroleum. This compound was first isolated by Carruthers and Cook (1954), and its identity was established by Barton *et al.* (1956). As suggested by Barton, the occurrence of this triterpenoid points to at least a partial vegetal origin of petroleum.



Agathenedicarboxylic acid

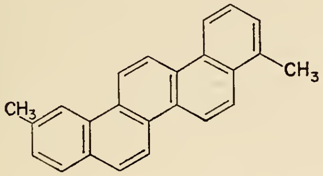
XX



Betulin

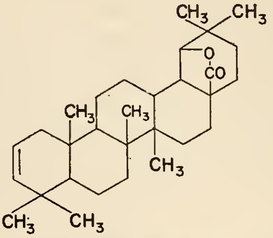
XXI

Steroids—A very important subdivision of the triterpenoids includes the sterols, which are formed in a biochemical synthesis through the elimination of three carbon atoms from a triterpenoid (C_{30}) intermediate. The sterols are common components of the unsaponifiable fractions of fats of plants and animals. Cholesterol (XXIVa) is the sterol most representative of higher animals, and sterols with additional carbon atoms in the side chain (XXIVb and XXIVc) are found in higher and lower plants and also in many of the invertebrates.



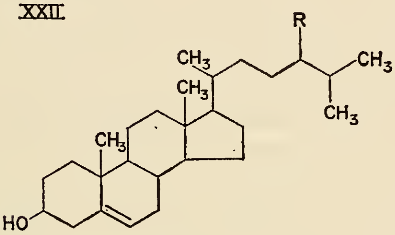
Dimethylpicene

XXII



Oxyallobetulene

XXIII



(a) R = H
(b) R = CH_3
(c) R = C_2H_5

Sterol

XXIV

The sterols are optically active compounds, and depending on the number and location of their cyclic double bonds, they may be strongly levo-rotatory, have but a feeble rotation, or be decidedly dextrorotatory. Petroleums also are optically active, as was first observed as early as 1835 by Biot, one of the pioneer investigators of optical rotation of polarized light (Biot, 1835). Walden (1906) was probably the first to connect the optical rotatory power of petroleum with a probable biological origin, and to compare it with other optically active organic fossil material, such as fichtelite, hartite, rhetenite and krantzil. Because of their wide distribution in fats, which might be regarded as source material of petroleum, the sterols have now and then been regarded as the parent substance of the optical activity of petroleum.

Koss (1911) was probably the first to provide experimental evidence for the occurrence of sterols in petroleum. He found that certain naphtha fractions of Javanese petroleum formed a precipitate when treated with an alcoholic solution of digitonin. Although the formation of a sparingly soluble digitonide is indeed characteristic for sterols, it is, however, not necessarily specific. At the same time Schreiner and Shorey (1911a) isolated a phytosterol, m.p. 135°, from soils in which it is present as an ester. More recently a mixture of β-sitosterol and stigmastanol associated with the triterpenoid friedelan-3β-ol has been obtained from peat (McLean *et al.*, 1958). This observation has quite recently been verified in our laboratory (Bergmann, 1958) with the isolation of β-sitosterylacetate from garden soil. Turfitt (1943) has estimated the sterol content of various types of British soil by means of colorimetry. The highest values up to 12.7 mg/kg of soil were obtained with soils of extreme acidity, poor aeration and excessive water content such as bog and fen peats. The same author also showed that cholesterol mixed with soil and buried in well-worked, loamy garden soil disappears at a rate of about 40% during the first six months, and about 60% within a year. The disappearance is at least in part due to the action of micro-organisms, such as *Proactinomyces*, which remove the sidechain and rupture the ring system of sterols (Turfitt, 1948).

The Rumanian investigators Cosmovici and Anastasiu (1936, 1937) extracted sterols or sterol-like crystalline products from a black shale and from Flysch sapropelites. The shale came from the Black Sea coast of Rumania and contained about 4–6% of organic matter consisting mainly of decomposition products of the alga *Cladophora cristalina*. The sapropelites were from Moldavia and abounded in the fossil remains of algae, fishes and crustaceans. Identification of the material was based on a color reaction and precipitation with digitonin both of which provide, if not convincing, yet strongly suggestive evidence for the presence of true sterols. Some tentative evidence for the presence of sterols in lignite and peat was obtained by Montignie (1938). Petroleum and asphalt (Aschheim and Hohlweg, 1933) and some medicinal waters and muds (Bragagnolo, 1949) possess noticeable estrogenic activity suggestive of the presence of steroid sex hormones. Inasmuch as many compounds structurally unrelated to the sex hormones show similar activity, this cannot be regarded as convincing evidence for the presence of steroids. Peruvian guano of undetermined age was found to contain 0.13% of a mixture of sterols (Krueger, 1944). In terms of a large guano deposit this represents a formidable amount of sterol. Because sterols are among the least water-soluble constituents of guano, its differential accumulation as other guano components are gradually being removed by solution can readily be visualized. Sterols are also present in the shells of certain molluscs, such as *Anadonta cygna*, to the extent of one part per thousand (de Waele, 1931). It is quite probable that protected by the calcium carbonate the sterol may survive geological periods, and that fossil shells may yet be found in which the presence of sterols can be demonstrated.

When cholesterol is heated either by itself or with substances such as aluminum chloride or activated carbon, an optically active mixture of liquid hydrocarbons is obtained. About thirty years ago this was regarded as evidence pointing to the role which sterols might have played in the formation of petroleum (Steinkopf, 1927; Zelinsky, 1927; Rakusin, 1928; Tsukamoto, 1928). Although this hypothesis has, on the whole, been found unacceptable, the probable occurrence of sterols and their degradation products in petroleum has not been discredited (Curphey, 1950). Thus some of the optically active fractions isolated from petroleum by

Oakwood and associates (1952), may have been derived from steroids as well as from sesqui- or triterpinoids. It is also conceivable that the chrysene derivative found by Carruthers and Cook (1954) in certain high boiling petroleum fractions owes its origin to sterols.* Many other hydrocarbons containing the phenanthrene skeleton may also have been derived from sterols. Even the formation of anthracene derivatives, which are not uncommon in Kuwait oil (Carruthers and Douglas, 1955), may be visualized as having been derived from steroids by means of the recently discovered anthrasteroid rearrangement (Burgstahler, 1957).

Adipocire and the Geochemistry of Triglycerides

Adipocire—Lipids composed of chemically resistant units are often found to remain long after death and decay have destroyed and removed other organic components of an animal organism. Gravediggers have long been familiar with the fact that in certain burial places human cadavers are in part converted into a material resembling spermaceti, the commercial wax from the sperm whale. One of the earliest and most descriptive references to this strange material is to be found in Sir Thomas Browne's *Hydrotaphia* (1658):

"In an Hydropicall (dropsical) body ten years buried in a Church-yard, we met with a fat concretion, where the nitre of the Earth, and the salts and lixivious liquor of the body, had coagulated large lumps of fat, into the consistence of the hardest castle-soap (Castile soap); whereof part remaineth with us." The existence of this remarkable material became known to the scientific world only after the distinguished French chemist, De Fourcroy, had attended as technical advisor the reorganization of the Cemetery of the Innocents in Paris during the years 1786–7. A few years later, De Fourcroy (1790) published an extensive report on his observations in this cemetery which had been in use for over three hundred years. He remarked that this material, which was later to be called adipocire, was most likely to be found in moist places where flimsy coffins had been stacked together in large numbers. In many instances this adipocire was the only organic matter to be found where the cadavers had been; accumulations were often in quantities larger than might reasonable have been expected from the original fatty parts of the body. De Fourcroy knew that the bodies buried there were those of the poor, the emaciated and diseased, containing but little fat, and he concluded that the fleshy parts of the body had contributed to the formation of the adipocire. The consistency of this wax changed from that of soft and pliable of relatively recent material to that of hard and brittle for the oldest.

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* Chrysene itself has been isolated from garden soil (Kern, 1947) in quantities of 15 p.p.m., which corresponds to about 40–50 lb/acre ft. Although it is possible that this compound was derived through rearrangement, degradation and dehydrogenation of naturally occurring steroids and triterpenoids, Cooper and Lindsey (1953) believe that this and other polycyclic hydrocarbons may be accounted for by precipitation from atmospheric pollution. These investigators found, for example, that 1 kg of snow containd 7–8 mg of pyrene.

Since then many findings of human and animal adipocire have been described. In all cases the cadavers seem to have either been buried in a rather wet place or to have been submerged in fresh or salt water for a number of years. Many of the older case histories have been recorded by Kratter (1907) and the more recent cases have been reviewed by Wasmund (1935). The question first raised by De Fourcroy as to whether or not the body fat is the sole source of adipocire has been re-asked many times during the last century and a half. It remains an important question and a definitive answer to it will be of great significance in future considerations of the geochemistry of fats. The theory that the fleshy parts, or the proteins, of the body contribute to the formation of adipocire has always had its vigorous supporters, and among them more recently Wasmund (1935) and Krejci-Graf (1935). There exists, however, a dearth of reliable experimentation in this field. Lehmann (1888) believed that he demonstrated convincingly that the amount of adipocire formed in a piece of meat suspended in water for nearly eight months was very substantially greater than the amount of fat originally present. The adipocire consisted in part of the calcium salts of fatty acids. In contrast Hecht (1934–5) suggested that during moist decomposition in the presence of air all protein is quickly converted to soluble material, and that only the body fat is converted into adipocire. Hecht also carried out experiments which he referred to as actuopaleontological studies. He buried bodies of sharks in the ocean bottom at various depths and found in all cases that the fats of the animals remained long after all proteins had disappeared. He also made the interesting and significant observation that the surviving fatty particles served as centers of concretions which gathered around them diverse particles, the fat moving from the center to the outside to furnish binding material for further growth of the concretions.

In the transformation of fats to adipocire the first step appears to be the hydrolysis of the fats, the disappearance of the water-soluble glycerol, and at least a partial hydration of oleic acid to hydroxy acids. Chevreul (1823) was the first to analyze adipocire and to show that it contained little if any glycerides but to consist mainly of solid fatty acids and their calcium salts. Among the saturated acids, palmitic acid is, as is to be expected, the most common. The amount of oleic acid is either quite small or zero in older samples of adipocire. In many cases its place has been taken by hydroxy acids which are certainly products of the hydroxylation of oleic acid. The following examples selected from many are illustrative of the origin and composition of adipocires. Wetherill (1856) described a sheep adipocire, 10 years old, which consisted of free fatty acids, and a sample from a fossil buffalo which consisted mainly of the calcium salts of fatty acids (fatty acids, 89.5%; calcium oxide, 10.5%). Ruttan and Marshall (1916) obtained the following analysis of an adipocire of undetermined origin: palmitic acid, 67.5%; stearic acid, 3.3%; oleic acid, 5.2%; hydroxystearic acids, 14.7%; calcium salts, 4.4%. A bird cadaver, investigated by Durand and Vieles (1937), weighed 282 g, of which 155 g or 55% was adipocire and the remainder bones, skin and membranes. The adipocire consisted of 80–90% free acids, mainly hydroxyacids, and the remainder glycerol and sterol. A very large amount of adipocire was discovered by Wells and Erickson (1933) in a wrecked boat load of herring which had remained submerged in 15 fathoms of water for an unspecified time. The material was composed largely of the calcium salts of saturated fatty acids.

The second step in the transformation of the fats appears to be the conversion of the fatty acids into calcium and magnesium salts. There exists good evidence that the calcium is not only derived from the water but also from the bones. Wiman (1941) examined two different adipocires and found one to consist almost entirely of free acids and another, taken from the sacrum, to contain 60% of calcium salts of fatty acids. He verified observations made by others that bones surrounded by or near adipocire are particularly brittle and decalcified. The slow process of the conversion of an animal fat into the calcium salts of fatty acids is probably best illustrated by observations recorded in a little-known article by Beetz (1843). He tells of a mine in Germany in which work had been discontinued for over one hundred years. When it was reopened, old candles were found which had been left in moist places, resting on formations rich in calcium carbonate. These candles which had originally been made from sheep's tallow were found to consist of a thick layer of a calcium salt (probably calcium palmitate) and a core of the unaltered glyceride. This is an important observation for it shows that the transformation of the fat to calcium salts of its fatty acids may occur under geochemical conditions and without the enzymatic processes of a decaying organism.

The fact that under certain conditions natural glycerides are converted to the calcium and magnesium salts of fatty acids raises the question of the occurrence of such salts in sedimentary rocks. There exists no uniformity of data on the solubilities of higher fatty acids and their calcium salts in water. In a comparative test, however, Langley *et al.* (1933) found free stearic acid to be between six and seven times more soluble at room temperature than calcium stearate. Calcium salts are but sparingly soluble in the organic solvents which are generally used to extract bituminous materials from rocks and soils, in contrast to the very ready solubility of the free acids. Such salts might, therefore, easily escape detection unless the rock sample is first acidified with mineral acid to free the organic acids. Aware of such possibilities, Faber (1933) and Faber and Krejci-Graf (1936) studied the solubilities of calcium stearate and palmitate. As expected, they found them to be soluble in ether or boiling benzene only with difficulty, and observed that only an exhaustive extraction with boiling toluene guaranteed their removal from mixtures. Using this procedure they then investigated a number of sedimentary rocks but found no convincing evidence for the presence of such salts. Nevertheless the possibility, if not the probability, of the occurrence of salts of fatty acids should always be considered, and a thorough analysis of the lipid-like contents of rocks and soils should include an extraction of the acidified material.

Recent Russian studies have shown that organic acids are far more common in sediments than was originally believed, and that more often than not they are present in form of their salts, as had already been suspected by Trask and Wu (1930). Verigo, as quoted by Shabarova (1954), isolated magnesium and calcium salts of fatty acids, including oleic acid, from ooze samples obtained from Black Sea coves. Shapiro (1952) found these and aluminum salts in extracts from muds of the Kuyalnitskii liman. Because the formation of contemporary marine deposits takes place at a slightly alkaline pH, Shabarova (1954) suggested that organic acids can only be present as their salts. Bogomolov (1954) holds that the bituminous fractions of organogenic, contemporary silts consist mainly of acids or their salts, and that hydrocarbons are present in but minor amounts. Comparative studies on free and bound bituminous material have been carried out by Strakhov and Rodionova (1954) who first extracted the rock samples exhaustively with petroleum ether, benzene, acetone and chloroform to obtain the free bitumen. The rocks were then treated with 10% hydrochloric acid, and re-extracted with chloroform and acetone to free the bound bitumen. Table 1 lists the relative amounts of the two fractions compared with humic acid and residual organic matter.

TABLE 1.

Free and Bound Bituminous Material from Rocks as Percentage of Total Organic Matter

Formation	Bitumen		Humic matter	Residual organic matter
	Free	Bound		
Silt (hard)	10.76	5.27	0.6	83.26
Argillite	6.39	4.40	0.37	88.24
Marl	13.02	6.58	trace	80.39
Limestone	48.0	27.0	none	25.0

All adipocires which have so far been chemically investigated are of a geologically insignificant age. It would be of great interest to learn what might happen to such material over a long span of years, whether it gets dispersed or accumulated, and what further chemical changes it will undergo if left undisturbed. There exist several reports on adipocire-like materials far older than any which have previously investigated. In his essay on the fossil elk of Ireland, Weaver (1825) reported that some of the bones of the *Euryceros* from the peat bogs of Rathcannon contained a marrow which looked like "fresh tallow". It might well represent an adipocire as old as 7000 years.* A fossil whale, of probable interglacial origin, was found to contain a "greasy" material with a fat to calcium oxide relationship of about 8:1 (Johnson, 1917). One of the oldest adipocires found *in situ* may well be the bituminous material in a remarkably well-preserved fossil egg from Arizona (Morgan and Tallmon, 1904). This egg, which is believed to be at least as old as the Quaternary, is filled almost entirely with crystallized colemanite. On the bottom and the sides of the inside of the egg, however, there is present some bituminous material. Its position in relation to the colemanite is thought strongly to indicate that the organic material was there before the mineral accumulated. Compared with the amount of fat in a duck's egg of the size of the fossil egg, one can conclude that all the bituminous material could easily have been derived from the fat alone. It is most unfortunate that in neither case have analyses been made which could offer such valuable information on the alterations of fats over long periods of time. Other, unfortunately even more fragmentary, information on unusual occurrences of material reminiscent of adipocire is contained in references to the "yellow and white fatty bodies" found on the bottom of the Black Sea (Archangelsky, as cited by Wasmund, 1935), the calcium salts of fatty acids occurring in the *Steinheimer Becken* (Klähn, as cited by Wasmund, 1935), the adipocires present in Cretaceous sediments (cited by Krejci-Graf, 1935) and the small brown lumps of partially crystalline lipids found in the beach mud of the Parnaiba Delta (Rolin, 1942).

Bog-butter—Closely related to the problem of the stability of fatty materials when interred in relatively moist surroundings is the old and discontinued art of preserving butter and other animal fats by keeping them in bogs. This method was practised mainly in Ireland and the Scandinavian countries. In Butler's Irish *Hudibras* (1663–1678) we read "Butter to eat with their hog, was seven years buried in a bog". It appears that the Irish placed large quantities of butter in wooden containers in bogs for further use. The butter would turn rancid, but eventually the more volatile fragments would disappear and the residual material would assume the consistency of tallow or cheese-like matter. Large quantities of this material, which became known as bog butter,† must have been forgotten or abandoned by their owners, and since the beginning of the last century many tubs of butter, weighing as much as 100 lb have been retrieved from old solid bogs at depths ranging from 10 to 12 ft (Wilde,

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[*] The writer has been informed by Mr. G. F. Mitchell of the University of Dublin that the Rathcannon skeleton is on exhibit in the National Museum of Dublin. Unfortunately there is no hope that the adipocire if still present could become a useful subject for analysis, for the bones have been preserved by periodic applications of petroleum jelly dissolved in paraffin.

[†] In the earlier literature no distinction is made between mountain tallow and bog butter. The former has also been found in bogs but it is essentially not saponifiable and hence more like hatchettite.

1856). One sample came from a vessel dated 1789 (Arup, 1932), but most of them appear to be of much greater antiquity, dating back to the eleventh and fourteenth century judging from the pyrographic markings on the vessels. The question as to whether the material was actually butter has been answered in the affirmative by the presence of cow hair. Among the analyses of bog-butter (Radcliffe and Maddocks, 1907; Arup, 1932) those by Ruttan and Howe (1921) are the most complete. These authors found bog-butter very similar in composition to adipocire. As in older samples of the latter, the original fat had been largely saponified and the water-soluble fragments, including acids of lower molecular weight, had been largely removed. The neutral fat in over a dozen different samples ranged from 6–26%, the average being 15%. The iodine values (average 13.44), coupled with the presence of an average of 15% hydroxy acids indicated that, as in adipocire, the oleic acid had disappeared or had become hydrated.

Tallow was similarly treated in other countries. Debes (1676) described how the inhabitants of the Faroe Islands took sheep tallow, allowed it to rot, then rendered it and "cast it into large pieces which they dig and put into moist earth to keep it, it growing the better the longer it is kept, and when it is old and is cut it tasteth like old cheese." The prosperous peasants would possess tallow dikes containing more than 100 loads of tallow. As yet, unfortunately, no analyses of such material have become available; its dating and analysis should supply further information on the conversion and geochemistry of triglycerides.

Closely related to the problems of the formation and alteration of adipocire and bog butter are Rubner's (1900, 1922) studies of the fate of fats in soils. In one series of experiments Rubner prepared 2–2.5% mixtures of butter in sterile and non-sterile soils of various composition. Under sterile conditions no significant decomposition took place, but hydrolysis occurred in untreated soils whether sandy or rich in humus. Even after 1 year, however, only 23% of the fat had disappeared and only 38% after 12 years. It appears, therefore, that under the conditions chosen, hydrolysis did not continue beyond certain limits, probably because the products formed were toxic in the processes bringing about the decomposition of fats. In the presence of an ample supply of calcium carbonate, hydrolysis of butter proceeded quite rapidly to form the calcium salts of the fatty acids. As noted, the occurrence in the poor soil, Elkton silt, of a triglyceride, possibly containing oleic acid, has been strongly indicated by the work of Schreiner and Shorey (1911c).

Beyond their saponification, the formation of salts of fatty acids, the oxidation of unsaturated acids, and the dissolution of all water-soluble moieties, little more is known about the geochemistry of the triglycerides (Zaloziecki, 1894). Most of the fatty acids or their salts will probably be completely degraded by microorganisms through processes such as β-oxidation. Others may be decarboxylated to hydrocarbons by microorganisms, a process well-known to occur also under anaerobic conditions

(Bach and Sierp, 1924; Seliber, 1926; Thayer, 1931; Rosenfeld, 1948). Such decarboxylations would lead to the natural, odd-numbered hydrocarbons. More recently, Shabarova (1954) has suggested the possible reduction of the salts of fatty acids under pressure and in the presence of sulfhydryl compounds. In such cases hydrocarbons might be formed with an *even* number of carbon atoms corresponding to the chain lengths of the original acids.

The formation of ketones by the dry distillation of the calcium salts of fatty acids is a well-known chemical reaction

$$(C_{17}H_{35}CO_2)_2Ca \rightarrow CaCO_3 + C_{17}H_{35}COC_{17}H_{35}$$

often accompanied by the formation of unsaturated hydrocarbons. Similar reactions may well occur in the geochemical alterations of fatty acids, in which, however, time would play a more important role than the heat suggested by Künkler and Schwedholm (1908). Subsequent reduction of such ketones could lead to hydrocarbons with an uneven number of carbon atoms and molecular weights similar to those of some of the recent and fossil hydrocarbons.

Consideration should be given to the general productivity of soils which have received or absorbed considerable quantities of fats, waxes and their transformation products, whether of animal or plant origin. Schreiner and Shorey (1908) and Schreiner and Lathrop (1910) isolated a fairly pure dihydroxystearic acid from soils in which it may be present in quantities of 200 lb/acre-ft. It was found mainly in soils of low fertility and since the acid is toxic, the authors believed its presence to be responsible for the poor quality of the soil. The dihydroxystearic acid may be viewed as having been formed by the oxidation of oleic acid, the most common of all the fatty acids. In a series of many papers, Greig-Smith (1910) has also attempted to explain soil exhaustion as the result of an accumulation of fats and waxes which he called *agrocire*. When this material is largely removed by solvent extraction, decomposition of other organic matter begins once more and with it the fertility of the soil is restored. Certain virgin soils investigated by Piettre (1923) were rich in a humus containing from 10–25% of fatty or waxy matter, but soils long exploited in coffee plantations contained humus at least half of which consisted of the fatty products which the author referred to as *les toxines du sol.* Incomplete as these old observations are, they do point to the possibility that an initial enrichment of soils or sediments by decomposition products of fats and waxes so reduces biological activity as to make possible the accumulation and geological survival of compounds the ancestry of which can be traced to the lipids of plants and animals.

Lignite and Peat Waxes

It has already been pointed out that the plant waxes which protect the surfaces of the leaves, needles, trunks and fruit of most of the higher plants belong to the least reactive and least water-soluble of compounds found in living matter. It is not surprising, therefore, that such waxes are capable of remaining essentially unchanged over long geological periods, and that they are found associated with fossil plant material. Many higher plants, in particular those belonging to the Coniferae and Myrtaceae, produce substantial quantities of compounds belonging to the family of terpenoids. These compounds also are relatively stable, but those of lower molecular weight are prone to polymerize into mixtures vaguely defined as resins or rosins. In fossil plant material the waxes and resins often occur together, but may be separated by a judicious use of solvents. The resins have so far yielded but few compounds, which have already been listed in the section on terpenoid compounds. Besides these substances there are the waxes, which are a mixture of higher alcohols and acids or their esters, higher paraffinic hydrocarbons and occasional amounts of ketones. All these compounds possess mainly, if not exclusively, straight chain structure.

Montan wax—Lignites are the most important sources of fossil plant waxes which, in composition, closely resemble the cuticular waxes of contemporaneous plants. One-fifth of the "paper coal" of Russia is said to consist of recognizable fossil cuticles which, when extracted separately, give 4% of a wax rich in free acids (Legg and Wheeler, 1929). In Central Germany lignite waxes are sufficiently abundant to make their recovery economically successful. When extracted with benzene such lignites yield from 20 to 25% of a crude wax called montan wax which may contain from one-fourth to one-half of less desirable resins. In special cases, such as *pyropissite*, now quite rare, the wax content may be as high as 75%. Such material is almost white, and merits special names such as "wax-coal" or "lipoliths". In certain German lignites there is interesting, visible evidence for a periodicity in the accumulation of such waxes. Layers alternate which are rich and poor in waxes, as readily differentiated by their color which is lighter the higher the wax content.

When von Boyen (1901), one of the pioneers in the technical use of montan wax, first applied for patents, they were rejected on the ground that this wax was but another example of the well-known mineral waxes, such as ozocerite. The patents were granted, however, when it could be shown that the wax was not merely another ill-defined mixture of hydrocarbons, but rather a complex mixture of free acids, esters and unknowns, which in a typical montan wax may occur in proportions of 17:53:30 (Pschorr and Pfaff, 1920). The bulk of the unknown fraction is resinous material.*

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* A more recent analysis reports the following percent-composition for crude montan wax (Presting and Steinbach, 1955):

liquid terpenes	0.12	paraffin	1.00
polyterpenes	3.41	wax alcohols	23.52
resin alcohols	1.43	wax ketones	2.32
resin acids	4.08	wax acids	47.76
oxidized resin acids	14.64	oxidized acids	1.00
stearin	0.10	lower fatty acids	0.11
ash	0.51		

The first studies on the more intimate, chemical nature of the wax originated toward the end of last century when Brückner (see Hell, 1900) reported the isolation from lignite wax of two acids and one ester, appropriately named geoceric and retinic acids, and geomyricin. These products were poorly identified and their names were soon forgotten. A few years later von Boyen (1901) isolated an acid which became widely known as montanic acid and which for many years remained a center of controversy. There were those who believed with Tropsch and Koch (1929) that its empirical formula was $C_{29}H_{58}O_2$, and others, like Holde *et al.* (1934), who held it to be $C_{28}H_{56}O_2$. The question was eventually settled by a synthesis of montanic acid which proved the natural material to be octacosanoic acid, $C_{28}H_{56}O_2$ (Piper *et al.*, 1934). The literature contains many references to the occurrence in montan wax of carboceric acid, $C_{27}H_{54}O_2$ (Tropsch and Kreutzer, 1922; Stadler, 1933). More exacting studies, however, have shown that such products lack uniformity, and that carboceric acid is in all probability but a mixture of montanic and lignoceric acids, $C_{24}H_{48}O_4$ (Francis *et al.*, 1930).

The unsaponifiable or neutral fraction of resin-free montan wax has yielded higher alcohols such as $C_{24}H_{50}O$, $C_{26}H_{54}O$ (ceryl alcohol) and $C_{30}H_{62}O$ (myricyl alcohol) (Pschorr and Pfaff, 1920). These alcohols have also been identified in contemporaneous plant waxes (Deuel, 1951). Of particular significance in montan wax is the presence of a ketone of rather high molecular weight, *montanone*, m.p. 59°, $(C_{27}H_{55})_2CO$ (Grün and Ulbrich, 1916–7). This ketone may be viewed as having been formed from two molecules of montanic acid by the loss of water and carbon dioxide.

Little is known about the hydrocarbon fractions of montan wax except for the presence of some unsaturated material (Grün and Ulbrich, 1929) and a series of poorly characterized compounds from $C_{19}H_{30}$ to $C_{30}H_{62}$, which Kraft (1907) obtained by high vacuum distillation.

Peat Wax—As may be expected, peat also contains significant quantities of a benzene-soluble wax. Irish peat wax was first investigated by Ryan and Dillon (1909) who separated it into 53% of an acid mixture containing mainly montanic acid, and 47% of unsaponifiable matter. The latter contained a non-alcoholic, oxygen-containing compound melting at 58–59°. It is quite probable that this compound was identical with montanone from lignite wax. The same authors also found another wax, *montanin*, which contained large quantities of sodium salts of fatty acids, the presence of which made the wax brittle. This extraordinary, and as yet unverified observation, is one of the very few references to the natural occurrence of "soaps" or sodium salts of fatty acids.

Reilly and his associates have extensively studied Irish peat wax, which they named mona-wax. It is somewhat softer and of a lower melting point than montan wax (Reilly and Emlyn, 1940). Hydrolysis of the wax yielded cerotic acid ($C_{26}H_{52}O_2$), the disputed carboceric acid (Reilly and Wilson, 1940), and behenic acid ($C_{22}H_{44}O_2$), which was particularly well characterized (Reilly *et al.*, 1943).

Analogous waxes have also been obtained from peats from many parts of the world. The Russian Tschischty sphagnum peat contains, according to Titov (1932), "carboceric" acid, an unidentified oxy-acid, a higher alcohol, $C_{27}H_{56}O$, of very questionable uniformity, and the hydrocarbons $C_{33}H_{68}$ and $C_{35}H_{72}$(15–20%). The wax also was found to contain resinous material consisting of esters of cyclic alcohols and cyclic acids. The wax fraction from the peat of the Rekinski swamps contained 57% of free acids, $C_{26}H_{52}O_2$ and $C_{28}H_{56}O_2$, and the remainder in form of esters and unsaponifiable matter (Rakowsky and Edelstein, 1932). Of similar composition are other Russian peat waxes (Roginskaya, 1936; Kuznetsov *et al.*, 1938), and those from Finland (Sundgren and Rauhala, 1949) and England (Cawley *et al.*, 1948).

The Lipids of Algae and Diatoms

Algae and diatoms have always been numbered among the most probable sources of solid and liquid fossil fuels. Most investigators agree with Brooks (1931) that the fats and waxes of these organisms are the original source material of petroleum, while others, such as Hackford (1932), hold it to be algal carbohydrates. This discussion is concerned only with the lipids of algae and diatoms and their transformations, a subject first discussed comprehensively by Seliber (1926) in a little-known Russian monograph. Only well-established chemical data and substantiated information will be covered.

Composition of lipids—In general the lipids of algae and diatoms do not differ particularly from those of other plants and many animals. The Japanese investigators Tsujimoto (1925), Takahashi *et al.* (1933–9), and Shirahama (1938) were the first to show that marine algae contain true fats, triglycerides, which are composed of the common saturated fatty acids from hexanoic to stearic acid, of unsaturated acids such as oleic and linoleic acid, and of the more highly unsaturated members of the series. Similar observations were made by Clarke and Mazur (1941), Mazur and Clarke (1942), Deuticke *et al.* (1949), Paschke and Wheeler (1954) and Low (1955) on the triglycerides of mono-cellular algae and diatoms such as *Chlorella*, *Scenedesmus* and *Nitzschia*.

Among the unsaponifiable fractions of algal lipids much attention has been given the diversity of sterols, among which fucosterol (Carter *et al.*, 1939), chondrillasterol (Bergmann and Feeney, 1950), ergosterol (Klosty and Bergmann, 1952), and quite recently also cholesterol (Tsuda *et al.*, 1957) have been identified. Since cholesterol has long been believed to be a typical product of animals, its isolation from several red, marine algae is of considerable importance. It is now no longer permissible *a priori* to equate a fossil occurrence of cholesterol with animal origin (see for example Trask and Wu, 1930). In the course of the isolation of the sterols some of the ubiquitous, solid paraffinic hydrocarbons were recovered as by-products. These were hentriacontane, $C_{31}H_{64}$, obtained from the common, brown alga, *Fucus vesiculosus* (Heilbron *et al.*, 1934), and from three species of green algae and one of red algae (Heilbron *et al.*, 1935), and pentacosane, $C_{25}H_{52}$, from the red alga, *Chondrus oscellatus* (Mori, 1943). As in other instances, these hydrocarbons are in all probability mixtures of homologs.

Shirahama (1938) appears to have been the first systematically to explore the non-steroid components of the unsaponifiable fractions of algal lipids. In a series of interesting but little known papers he describes the isolation of alcohols, of some interesting hydrocarbons, such as $C_{18}H_{36}$ and $C_{20}H_{34}$, and of unsaturated, optically active terpenes. These observations have found support in the more recent work by Takaoka and Ando (1951), who isolated a liquid from the steam-distillable fraction of the oil from the alga, *Dictyopteris divaricata*, which was found to contain sesquiterpenes and sesquiterpene alcohols. Among these, cadinene (XII) and (—)-cadinol were definitely identified. A similar study, carried out under the direction of Whitmore (1946), involved the solvent extraction of fresh-water algae and marine kelps, and the isolation and separation of their hydrocarbon fractions. No definite compounds were isolated, but a complex, optically active, mixture of distillable hydrocarbons ranging in molecular weight from 225 to 435, and of a residual material containing probably more than thirty-four carbon atoms was obtained. A ketone, heptadecanone-2, $CH_3(CH_2)_{14}COCH_3$, has been isolated from the brown marine alga, *Zonaria zonalis* (Klosty, 1952).

All constituents that have so far been isolated from the lipid and terpene fractions of algae and diatoms are also more or less common components of most other terrestrial and aquatic plants. Of particular interest is a study by Lovern (1936), an investigator with comprehensive experience in comparative chemical studies of fats. He analyzed mixtures of fatty acids from several green, brown and red algae, and compared them with those obtained from other, well-known fats. No significant differences were observed between the fats of fresh-water and marine species. The fats of all green algae, of a pond weed, higher plants and a diatom were all of a similar type and reminiscent of the fats of fresh-water animals. Only the fat of a red alga approximated the composition of the fat of a marine animal, particularly in the presence of substantial quantities of unsaturated fatty acids of the order C_{20} and higher. Differences in the composition of algal fats appear, therefore, to follow botanical lines rather than to depend upon the medium in which the algae live.

Accumulation of lipids. Although there are no extraordinary differences in the composition of algal fats, great variations have been reported in the total lipid content of algae. Some observed differences may well result from differences in the techniques employed in the extraction of the lipids. It must also be borne in mind that the fats are contained largely within the cells of the plants, and that the cell membranes are not easily broken down by mere solvents. This is particularly true for monocellular algae and diatoms. Geoghegan (1951) obtained only 1–5% of soluble material on extraction of the alga *Chlorella* with ether, but considerably more material was obtained after preliminary treatment of the cells with dilute hydrochloric acid, an agent capable of destroying the cell walls. Standard procedures that have been used in the extraction of algae are those by Milner (1948) and Belin (1926). To ensure complete recovery of the unsaponifiable material, it may be necessary to saponify the entire organism and to extract the mixture thus obtained with ether. In the case of diatoms, however, this method may lead to silicate solutions, which are difficult to handle.

By the use of standardized extraction procedures, it has been shown quite convincingly that there exists a relationship between the fat content of various species of algae and their habitat. Russell-Wells (1932) first observed that among different species of littoral marine algae the fat content was highest, (8.0%) in the free-floating, often desiccated *Pelvetia libera*, medium in the less-exposed *Pelvetia caniculata* (4.9%) and *Fucus vesiculosus* (2.6%), and lowest (0.3%) in the deep-sea weed, *Laminaria digitata*. Conversely the unsaponifiable fraction of the fat increases from 7.6% for the most exposed form, to 26% for the most submerged.

The possible accumulation of large quantities of fats by algae has been of considerable interest for two widely separate reasons. One is based on the search for a new, fast growing source of fats suitable for human and animal nutrition (Burlew, 1953); the other, because vast accumulations of algal material have been shown to be the source of certain types of coal, and have been suspected of having played a role in the formation of petroleum. Although certain investigators have believed that the accumulation of fats is a characteristic of certain classes of algae, Collyer and Fogg (1955) have recently furnished important evidence testifying to an interesting relation between the fat content of an alga and the environment of the species. It had already been found by Barg (1943) that the fat production of diatoms, such as *Nitzschia* and *Pinnularia*, is markedly increased by unfavorable environment. Under such conditions two-thirds of the cell lumen of the organism may be filled by fats, and the original cell sap may have all but disappeared. In the case of *Chlorella*, Milner (1948) found that the lipid content, as determined by his special method, may be increased from 20 to 77% by alteration of the conditions under which this unicellular alga is grown.

Collyer and Fogg (1955), however, were the first systematically to explore such relationships. Their careful studies included representatives of six classes of algae. It was found that, while the fat content of *Chlorella* may indeed be varied by changes in any one of several factors, the variations are limited by the concentration of available nitrogen in the medium. Only when available nitrogen falls below a certain level does fat accumulation become considerable. At about the same time similar observations were made by Iwamoto and associates (1955). They also noticed an inverse relationship between the nitrogen and lipid content of *Chlorella.* When grown on a nitrogen-deficient medium the crude protein content of this alga was found to drop from 44.5 to 9.9% while the lipid content rose from 18.5 to 63.7%.

Another factor which appears to be of very great importance in fat accumulation is water deficiency. The observation by Russell-Wells (1932) that the most exposed of the marine littoral algae are the richest in fat supports this view, as do the much older findings by Lüders (1862) on the accumulation is water deficiency. The observation by Russell-Wells (1932) drying of yeast its fat and steroid content undergo a rather striking increase (Halden, 1934). Both Heide (1939) and Collyer and Fogg (1955) have concluded that deficiency of nitrogen and a decreasing availability of water independently promote the accumulation of fat, and it appears from the available data that the latter effect is the more striking. It is quite possible that the very high fat contents found in *Chlorella* by Milner (1948) may at least in part have been caused by the desiccation of the living material under conditions known to induce fat accumulation. Other factors such as deficiency of phosphate, magnesium, potassium (Spoehr and Milner, 1949), temperature and supply of carbon dioxide are without perceptible effect (Collyer and Fogg, 1955).

As yet no attention seems to have been called to the possibly significant relationship between the accumulation of fats in algae and diatoms, induced by changes in the environment, and the content of bituminous material in fossil algal remains. One such substance, which is particularly rich in extractable lipoid matter, is the *coorongite* formed in salt water lagoons not far from Coorong in Australia. Thiessen (1925) found that in these and other lagoons in the vicinity there is an abundant growth of an alga, *Elaeophyton coorongiana*, rich in fatty oil. Seasonally the lagoons become covered with a very thick layer of algae which eventually collects at the shores there to dry into a brownish mass. One sample upon extraction with carbon bisulfide gave as much as 70% of its dry weight in form of a viscous yellow oil, and another sample afforded 24% of a yellow unsaponifiable wax melting between 35° and 42°. A more detailed analysis of Thiessen's *coorongite* was carried out by Stadnikov and Weizmann (1929) who found this brown, soft and rubbery material to contain 57% of a petroleum-ether soluble oil which, upon saponification, gave 16% of fatty acids that were solid at room temperature, and a complex mixture of unsaponifiable matter. Similar algal blooms have been reported from many parts of the world such as on the Wannsee Lake near Berlin (Marcusson, 1925) and the world famous "diatomaceous soup" in Walfish Bay off the West Coast of Africa. More closely related to coorongite is the accumulation of algal matter on the shores of Lake Ala-Kul, a flat, somewhat brackish section of the Lake Balkshash in the Asiatic Russian district of Kazak, A.S.S.R. At certain times of the year this lake supports an enormous quantity of the oil-bearing, planktonic, green alga, *Botrycoccus Braunii K.*

(Salesky, 1914; quoted from Stadnikov and Woldschinskaja, 1930). Periodically the algal mass is washed ashore where it turns into a yellow-brown rubbery material, balkshashite, which contains almost 20% of a benzene-soluble wax. Upon treatment of the benzene-insoluble residue with dilute sodium hydroxide (2%) at room temperature, there is obtained a solution which, upon acidification, yields an ether-soluble precipitate representing almost one-half of the starting material. Upon standing this material hardens to the consistency of vulcanized rubber. This observation, coupled with others made by Stadnikov and associates,lends some credence to his contention that algal fats undergo saponification followed by polymerization of the resulting unsaturated fatty acids, and that coorongite and balkshashite are but steps in a geochemical process similar to that which lead to the formation of boghead coal (Stadnikov and Kaschtanov, 1929). A similar concept is referred to in Wolansky's (1933) review of Russian studies of sedimentation in the Black Sea. Wolansky quotes Archangelski's views on the cyclic growth of phytoplankton, its deposition in layers, and the hypothetical, petroleum producing organism, *Micrococcus petroli.*

The high oil and wax content of coorongite and balkshashite is probably associated with the periodicity of the algal growth. As the algal colonies increase in size, they make ever heavier demands upon the nitrogen supply of the water, and its decrease is accompanied by an increase of the algal fat content. When toward the end of the season the colonies are washed ashore, they may well undergo a second increase in fat content during the period of desiccation preceding the death of the organism. Under such conditions the lipid content may well reach figures as high as those observed in old laboratory cultures of algae.

Two rather old papers by Krämer and Spilker (1899, 1902) are of considerable interest in this connection in as much as they deal with a 40 ft thick layer of a greyish-brown, crumbly material, fatty to touch, which had formed in a former lake in Northeast Germany. The solid matter of the mass consisted mainly of shells of diatoms, and its ash content was 76.3% SiO_2. Extraction of the material with toluene after boiling with dilute hydrochloric acid yielded 3.6% of a wax-like substance. This material proved to be quite different from fossil hydrocarbons such as ozocerite in being capable of saponification, and its composition was reminiscent of that of plant and lignite waxes. Among unknown saponification products were saturated acids in the range of C_{20}, C_{22} and C_{24}, and saturated alcohols in the range of C_{20} and C_{22}. The diatomaceous or infusorial earth of commerce has long been known to contain a wax that is extractable with organic solvents (Andés, 1918; Charrin, 1939). Because diatomaceous earth is an adsorbing material, it is possible that the wax contained in it is of exogenous origin. An endogenous formation, however, is by no means excluded, and it is to be hoped that a comparative chemical study of fossil and recent diatom lipids may eventually provide an answer to this interesting problem.

Lipids of Marine Animals

Fishes—In 1923 Macfarlane published his interesting book *Fishes, the Source of Petroleum*, an erudite summary and interpretation of data then known in support of a hypothesis whose roots reach back over one hundred years into the studies of Murchison (1829), Dufrenoy (1847), Posepny (1865), and others. The scope of this discussion permits neither a critical evaluation of Macfarlane's work nor resumé of our present state of knowledge of the fats and oils of fishes. For economic reasons the lipids of fishes have been studied extensively during the past several decades and they have been reviewed in monographs by Lovern (1942) and Hilditch (1956). This review will be restricted to a summary of a few interesting facts that have come to light since publication of Macfarlane's book.

In discussing the fats and oils of fishes cognizance must be taken of the fact that the livers of many fish, in contrast to those of land animals, are quite rich in lipids, and that they often serve as the principal fat depot of the fish. It is in the liver, therefore, that the bulk of the lipids of fishes is concentrated. Many liver oils are mainly composed of triglycerides, and they consequently contain only 1 or 2% of unsaponifiable matter such as cholesterol. Other fish, however, contain liver oils with rather high quantities of unsaponifiable matter. Thus the liver oil of the ratfish, *Chimaera monstrosa*, yields 37% of unsaponifiable material consisting mainly of selachyl alcohol,

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2{-}O{-}CH_2CHOHCH_2OH,$$

and batyl alcohol,

$$CH_3(CH_2)_{16}CH_2{-}O{-}CH_2CHOHCH_2OH,$$

(Hilditch, 1956). These glyceryl ethers are somewhat more water soluble than the acids and alcohols of the same chain length into which they are probably easily converted by microbial processes. Other liver oils, such as those from *Lotella phycis* and *Laemonemia morosum* (Komori and Agawa, 1954), may yield upon saponification as much as 18% of the higher alcohol, 11-docosenol, $CH_3(CH_2)_9CH{=}CH(CH_2)_9CH_2OH$, which is also found in sea anemones and plankton oil (Bergmann *et al.*, 1956).

Most interesting are the liver oils which consist mainly of unsaponifiable matter, 50–90%, which contains mainly hydrocarbons. An outstanding example is a deep-sea shark from Formosa whose liver oil consists of 87.5% unsaponifiable matter containing 84% hydrocarbons (Hata and Kunisaki, 1940). The hydrocarbons are not of the familiar straight-chain variety but are similar to acyclic terpenoids among which the triterpenoid squalene (III) is the most typical representative. As a rule this substance is accompanied by smaller amounts of terpenoid hydrocarbons of lower molecular weight such as pristane, 2,6,11,14-tetramethylpentadecane (Pliva and Sörensen, 1950), and zamene, 2,6,11,14-tetramethylpentadec-1-ene (Cristensen and Sörensen, 1951). It is reasonable to assume that the geochemistry of liver oils so rich in hydrocarbons is quite different from that for oils containing triglycerides. Such liver oils are, however, not common to most fish, but are restricted to the Elasmobranchii, and even within the families of sharks their occurrence is limited and rather erratic.

Invertebrates—Contrasted with the wealth of information on the fats and oils of fish and other aquatic vertebrates, our knowledge of the lipids of marine invertebrates is quite fragmentary. Only in recent years have data become available which may well prove to be of geochemical interest. The most characteristic difference between the total lipids of vertebrates and invertebrates is the presence in the latter of substantial quantities of unsaponifiable material. Except for some special cases such as the aforementioned shark-liver oils or of *spermaceti*, vertebrate fats on the average yield less than 2% of unsaponifiable matter and are composed predominantly of triglycerides. As shown in Table 2, the unsaponifiable fraction of invertebrate lipids is quite substantial and is generally higher the more primitive the animal form which it has been derived (Bergmann, 1949). This holds true regardless of the habitat of the invertebrate; planktonic, pelagic or sessile.

TABLE 2.
Unsaponifiable Matter of Invertebrates

Phyla	Unsaponifiable % of total lipids (average)	Number of species examined
Protozoa	35	2
Porifera	37	45
Coelenterata	35	25
Annelida	22	7
Crustacea	16	14
Mollusca (marine)	13	32
Echinodermata	19	20

Such high contents of unsaponifiable material signify that approximately only half of the total lipids of invertebrates consist of triglycerides, the remainder being represented by waxes, sterols and unknown components. Waxes are particularly prominent among the coelenterates, this being best illustrated by the lipids of *Condylactis gigantea*, a sea anemone which is quite common along the coral growths of Bermuda and the Bahamas (Bergmann *et al.*, 1956). Like many other sea anemones, it is extraordinarily rich in lipids, containing them up to nearly one-third of its dry weight. The total lipids are solid, and they may be divided chromatographically into about equal parts; triglycerides consisting principally of palmityl myristate, and a wax, which is a mixture of myristyl myristate ($C_{14}H_{29}OCOC_{13}H_{27}$), myristyl palmitate ($C_{14}H_{29}OCOC_{11}H_{31}$), and cetyl palmitate ($C_{16}H_{33}OCOC_{15}H_{31}$). Saponification of the total lipids yields higher alcohols to the extent of about 25%.

Such waxes, and in particular cetyl palmitate, are among the most conspicuous and the most readily isolated components of coelenterates. They separate as nicely crystalline fractions from the acetone extracts of coelenterates whether they are solitary or colonial anemones (Bergmann *et al.*, 1951), solitary or reef-building corals (Bergmann and Lester, 1941), or the carbonaceous, polyp-bearing layers of gorgonias (Kind and Bergmann, 1942).

Coral reefs—The presence of lipids in reef-building corals is of particular interest. Contrary to popular belief, corals contain significant quantities of organic matter, from 2 to 8%. This fact was first reported by Silliman (1846) in his classical paper on the composition of corals, and it was more recently substantiated by Clarke and Wheeler (1922) for twenty-eight species. Silliman was also the first to mention the presence in corals of a sebaceous material. Boiling of coral fragments with water separated this substance from its surroundings, and made it rise to the surface of the water in the form of droplets which, upon cooling, assumed a Vaseline-like consistency. One hundred years later this wax was investigated by the writer and his associates and was found to be present in Bermuda corals to the extent of about 0.3%, and in corals from more tropical waters up to 0.5%. As had already been indicated by Silliman, these lipids are not solely confined to the relatively thin, living layer of corals, but extend deep into the entire structure. The composition of the lipids is quite similar to that of anemone extracts, with triglycerides and cetyl palmitate being the principal components (Bergmann and Lester, 1941).

In 1940, Bergmann and Lester suggested that reefs, whether built by corals, bryozoa or coralline algae, might be regarded as vast accumulators of lipids which are entrapped in the ever expanding reef and thus removed from circulation. They also suggested that past accumulations of this type may have served as sources of petroleum. If under special circumstances the reefs should not be destroyed and their organic matter not be extracted by boring organisms such as worms and molluscs, the coral lipids, triglycerides, and waxes may be expected to be hydrolyzed and the acids converted into their calcium salts in a matter similar to that in the formation of adipocire. This is a challenging problem capable of partial solution through judicious studies on recent coral reefs.

For many years a relationship has been visualized between living coral reefs and the active formation of bituminous material. During his travels through the Red Sea, Fraas (1867) was impressed by the fact that during the great heat of the day living reefs would exude droplets of petroleum-like material. His observations were supplemented by those of others and particularly by Sickenberger (1892), who discussed sections of the Red Sea which, surrounded by reefs and protected from wave action, abounded in invertebrate life. He became convinced that in many such pools the forces of life producing new organic matter were out of balance with those consuming the old. The unconsumed cadavers then underwent a decomposition which Sickenberger called a "petroleum fermentation", which is accompanied by vigorous evolution of hydrogen sulfide. The surface of such undisturbed pools then gets covered with layers of oil up to 10 cm thick. Sickenberger believed that this oil eventually became absorbed by the porous coral rock. Assuming such observations to be fundamentally correct, coral reefs might act as the receivers and accumulators of exogenous bituminous material rather than of the endogenous material postulated by the hypothesis outlined above. Here, also, comparative studies of the chemistry of invertebrate decomposition and the composition of the oil "exuded" from coral reefs should go far in evaluating this hypothesis.

Sponge hydrocarbons and other compounds—As yet little is known about the hydrocarbons of marine invertebrates. Only in the case of sponges have they been searched for in a somewhat systematic manner. In a series of papers the writer and his associates have shown that sponges are relatively high in lipids (Bergmann, 1949), and that these in turn give rich yields of unsaponifiable matter which contains substantial quantities of sterols of astonishing structural diversity. In addition, there are present other alcohols and ketones, as yet poorly characterized, as well as hydrocarbons. Solid hydrocarbons of the order of $C_{27}H_{56}$, $C_{29}H_{60}$ and $C_{31}H_{64}$ have been obtained from seven species of sponges, and their occurrences in other sponges may be regarded as certain (Feeney, 1952). More interesting are the liquid hydrocarbons that have so far been isolated from five species of sponges in yields of from 2–5% of the total unsaponifiable fraction. These hydrocarbons have molecular weights in the range of 230–320, are slightly levo-rotatory, and possess infrared spectra indicating considerable methyl branching. It seems probable that principal constituent of this hydrocarbon mixture is the terpenoid hydrocarbon pristane (2,6,11,14-tetramethylpentadecane), which had previously been found in shark-liver oil (McAleer, 1954). Subsequent studies in the author's laboratory have shown that mixtures of straight-chain and terpenoid hydrocarbons are found among the lipids of nearly all marine invertebrates.

Batyl and selachyl alcohols, first discovered in shark-liver oils, are commonly found in the unsaponifiable fractions of invertebrate lipids. Lower alcohols are also occasionally observed, and 7-decen-1-ol was recently isolated from a seasquirt (ascidian) by Kita (1957). It is of some interest that this alcohol has an odor reminiscent of that of "low tide". Illustrative of the diversity of chemical synthesis in marine invertebrates is the presence in sponges of the aromatic, unsaponifiable ethers, anethole ($CH_3OC_6H_4CH{=}CHCH_3$), and methylchavicol ($CH_3OC_6H_4CH_2CH{=}CH_2$) (Bergmann and McAleer, 1951). These compounds had previously been regarded as typical plant product. Carcinogenic hydrocarbons such as 3,4-benzpyrene have been isolated from barnacles by Shimkin *et al.* (1951). These substances were probably of exogenous origin having been derived from petroleum waste: barnacles from unpolluted waters were devoid of such hydrocarbons.

In evaluating the diversity of chemical synthesis in marine invertebrates sight should not be lost of the fact that many of these animals live in symbiosis with monocellular algae. The presence of the algae is often apparent from the green color of the organism, and traces of chlorophyll or its degradation products are often encountered in extracts from invertebrates. The presence of such pigments in bituminous materials therefore does not constitute a conclusive proof of their vegetable origin.

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CHAPTER 13

ORGANIC GEOCHEMISTRY OF SULFUR*

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Introduction

Sulfur, both free and combined with other elements, is widely and abundantly distributed in nature. It is ranked by Urey (1952) as being tenth in cosmic abundance. By weight, sulfur is believed to be the fifth most abundant element in the planet Earth, although only thirteenth in abundance in the upper 10 km of the Earth's crust (see Table 1). It is sixth in abundance in the sea, where it makes up 1.56% of all dissolved solids. Sulfur is among the ten most abundant elements in biological materials, being essential for all known living organisms as a constituent of proteins and many other compounds, organic as well as inorganic. In certain microorganisms sulfur substitutes to a limited extent for oxygen as a hydrogen acceptor, leading to speculation concerning the possibility of sulfur replacing oxygen in living organisms on other planets. In various combinations with oxygen, hydrogen, and other elements, sulfur forms strong acids and/or reducing agents, which have far-reaching effects on physicochemical conditions influencing geochemical cycles and the activities of living organisms.

Having oxidation states ranging from -2, as in sulfides (S^{2-}), to $+6$, as in sulfates (SO_4^{2-}), sulfur occurs in a great variety of chemical combinations. Intermediate oxidation states are represented by sulfur dioxide (SO_2), sulfites (SO_3^{2-}), thiosulfates ($S_2O_3^{2-}$), polysulfides (MS_n), and polythionates (MS_nO_6), where n may be any value from 2 to 6 and M is a mineral cation. With the exception of sulfates, the anions of oxyacids of sulfur rarely occur in nature except at relatively low concentrations in transitory states. Under certain conditions sulfur combines directly with hydrogen and with nearly all metals to form sulfides. In magma and igneous rocks sulfur is believed to be present primarily in the form of sulfides. Sulfate is the predominant form of sulfur in the hydrosphere and in the biosphere, where the state of this element is modified in many ways by organisms. Both plants and animals bring about the regrouping of atoms, resulting in changes in chemical composition of sulfur compounds. Microorganisms, and perhaps higher organisms also, fractionate isotopes of sulfur. Biological agencies contribute to the weathering of sulfur-bearing

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* Chapter submitted in 1959.

TABLE 1.

Elements Arranged in Order of Abundance (per cent by weight) in Various Materials

Rank	Whole Earth[1]	Earth's crust[2]	Sea water[3]	Marine copepod[4]	Human body[5]
1	Fe 35.39	O 46.60	O 85.88	O 66.65	O 63.03
2	O 27.79	Si 27.72	H 10.72	C 15.37	C 20.20
3	Mg 17.00	Al 8.13	Cl 1.898	H 8.39	H 9.90
4	Si 12.64	Fe 5.00	Na 1.056	N 3.85	N 2.50
5	**S 2.74**	Ca 3.63	Mg 0.127	Cl 2.68	Ca 2.50
6	Ni 2.70	Na 2.83	**S 0.0884**	Na 1.38	P 1.14
7	Ca 0.61	K 2.59	Ca 0.0400	K 0.74	Cl 0.16
8	Al 0.44	Mg 2.09	K 0.0380	**S 0.35**	**S 0.15**
9	Co 0.20	Ti 0.44	Br 0.0065	P 0.33	F 0.13
10	Na 0.14	H 0.14	C 0.0035	Ca 0.10	K 0.11
11	Mn 0.09	P 0.118	Sr 0.0013	Mg 0.08	Na 0.10
12	K 0.07	Mn 0.100	B 0.0004	Br 0.02	Mg 0.07
13	Ti 0.04	**S 0.052**	Si 0.0002	Si 0.02	Fe 0·01
14	P 0.03	C 0.032	F 0.0001	Fe 0.02	
15	Cr 0.01	Cl 0.031	Al 0.0001		

[1] From data compiled by Mason (1958).

[2] Rearranged from data compiled by Rankama and Sahama (1949).

[3] Calculated from data given by Sverdrup *et al.* (1942).

[4] Calculated from data given by Vinogradov (1953).

[5] From Lotka (1924).

rocks and to the transposition of sulfur between the lithosphere, hydrosphere, atmosphere, and biosphere. By their effects on the cycles of oxygen, carbon, hydrogen, iron, and certain other elements, organisms may alter the state of sulfur. Polynov (1937) characterizes these intermeshed processes, some of which are not fully reversible, as being polycycloid.

The general trend in the transformation of sulfur is toward a more stable state. According to Urey (1952), at temperatures below 1160°K, hydrogen sulfide is stable relative to free sulfur. He points out that in the presence of excess atmospheric hydrogen, sulfur will be present as hydrogen sulfide when thermodynamic equilibrium obtains. In intimate contact with ferrous iron, iron sulfide will be formed, this being the stable form of sulfur at 1 atm and 298°K in the absence of atmospheric oxygen. In the presence of excess oxygen, sulfur will be present as sulfur trioxide, assuming thermodynamic equilibrium. In intimate contact with water or silicates, oxidized sulfur will be present as sulfates. Of course, thermodynamic equilibrium never obtains exactly, so it is not surprising to find sulfur occurring in several different states of oxidation in the weathered crust of the earth, particularly since there may be considerable difference in conditions and in the concentration of reactants from place to place. Even endothermic reactions, such as sulfate reduction or the synthesis of organic sulfur compounds, for example, may take place in the biosphere, the necessary energy being supplied by sunlight and/or by the oxidation of other materials in coupled reactions catalyzed by living organisms.

Occurrence and Transformation of Juvenile Sulfur

Juvenile sulfur occurs largely as mineral sulfides with lesser quantities of sulfosalts, sulfates, hydrogen sulfide, sulfur dioxide, and elemental sulfur. Hydrogen sulfide should always have been present in only small amounts, according to Urey (1952), because of the high stability of iron and other metallic sulfides. The appearance of sulfates and other sulfoxy compounds would be expected only with the advent of a highly oxidizing atmosphere. Urey believes that reducing conditions may have maintained on the earth until some 8×10^8 years ago.

Analyses presented by Clarke (1924) indicate that sulfur in igneous rocks is contained almost quantitatively in metallic sulfides, the most abundant being pyrite (FeS_2), pyrrhotite (Fe_5S_6–$Fe_{16}S_{17}$), chalcopyrite ($CuFeS_2$), pentlandite ($FeNiS_3$), and bornite (Cu_5FeS_4). Sphalerite (ZnS), galena (PbS), molybdenite (MoS_2), argentite (Ag_2S), cinnabar (HgS), chalcocite (Cu_2S), and many other metallic sulfides are found in a few localities in limited amounts, often as secondary intrusions. Troilite (FeS) occurs commonly in iron meteorites (see Chapter 1) and sparingly in igneous rocks on the earth. Bournonite ($2PbS.Cu_2S.Sb_2S_3$), pyrargyrite ($3Ag_2S.Sb_2S_3$), and stannite ($Cu_2S.FeS.SnS_2$) are representative of several species of sulfosalts which are occasionally found in relatively small amounts associated with primary minerals probably of late origin (Dana and Ford, 1932). Sulfosalts differ from sulfides in that sulfur takes the place of oxygen; for example, zinkenite ($PbSb_2S_4$) is a salt of the theoretical acid $H_2Sb_2S_4$. Of rare occurrence in igneous rocks are silicate sulfates such as haüynite ($3NaAlSiO_4.CaSO_4$) and noselite ($3Na_2Al_2Si_2O_0.Na_2SO_4$). Little is known regarding the occurrence, age, or mode of formation of sulfur dioxide or free sulfur in igneous rocks, although both are associated with volcanoes, which are believed to contribute substantially to the sulfur content of soil, sea water, and sediments (Rubey, 1951).

Gaseous exhalations from volcanoes and fumaroles generally contain hydrogen sulfide and/or sulfur dioxide (Clarke, 1924; Shepard, 1938). Sulfur vapor and sulfur trioxide are sometimes present in samples of such exhalations. Zies (1938) estimated that fumarole gases from the Valley of Ten Thousand Smokes emitted 0.3×10^6 metric tons of hydrogen sulfide per year. Free sulfur may be formed by the partial oxidation of hydrogen sulfide by atmospheric oxygen:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S.$$

In the presence of water or certain catalysts, hydrogen sulfide reacts with sulfur dioxide to yield free sulfur (Jacobson and Hampel, 1958):

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S.$$

Sulfur dioxide unites with water to form sulfurous acid, which may be oxidized by atmospheric oxygen to sulfuric acid:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4.$$

When exposed to sunlight and moisture, sulfur dioxide may be decomposed with the formation of sulfur trioxide and free sulfur:

$$3SO_2 + h\nu \rightarrow 2SO_3 + S.$$

Sulfur trioxide unites with water to give sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

Sulfuric acid may also be formed by the action of atmospheric oxygen on free sulfur in the presence of moisture:

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4.$$

In soil, water, and sediments, certain microorganisms oxidize sulfur or it may be slowly oxidized spontaneously in the zone of weathering. Sulfuric acid usually occurs in nature in very dilute aqueous solution, although it is sometimes a cause of extreme acidity. Values more acid than pH 3.5, for example, have been recorded in some crater lakes, and bogs (Hutchinson, 1957). The weathering of pyrite is believed to be a major source of sulfuric acid in nature:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4.$$

Sulfuric acid from the foregoing and/or other reactions tends to liberate hydrogen sulfide from certain metallic sulfides, for example:

$$PbS + H_2SO_4 \rightarrow PbSO_4 + H_2S.$$

The hydrogen sulfide may be carried away by solution in water, it may escape temporarily into the atmosphere, and/or it may be oxidized with the formation of sulfur and sulfuric acid. Sulfuric acid combines with other basic metals to yield sulfates, the most abundant form of sulfur in the hydrosphere and regolith. The movement of sulfuric waters through lime-bearing rocks tends to convert carbonates into calcium sulfate:

$$H_2SO_4 + CaCO_3 \rightarrow H_2CO_3 + CaSO_4$$

this being representative of one more of the many ways in which metallic sulfates are formed in the zone of weathering. Through processes of recombination, base exchange, evaporation, hydration, etc., gypsum ($CaSO_4.2H_2O$), barite ($BaSO_4$), celestite ($SrSO_4$), anglesite ($PbSO_4$), astrakhanite ($Na_2SO_4.MgSO_4.4H_2O$), kainite ($KCl.MgSO_4.3H_2O$), kieserite ($MgSO_4.H_2O$), glauberite ($Na_2SO_4.CaSO_4$), anhydrite ($CaSO_4$), mirabilite ($Na_2SO_4.10H_2O$), and many other sulfates are formed. Although some of these minerals are sparingly soluble and relatively stable under ordinary conditions, they may be slowly dissolved to be carried away by water or reduced to other forms of sulfur in the biosphere.

Calcium sulfate is precipitated from evaporating sea water mainly as anhydrite ($CaSO_4$) because high osmotic pressure of brine prevents the formation of the dihydrate, gypsum. Gypsum is formed later when anhydrite absorbs atmospheric water. Formed along with gypsum in marine evaporites is polyhalite ($K_2SO_4.2CaSO_4.MgSO_4.2H_2O$).

Occurrence and Abundance of Sulfates

Besides constituting a great reservoir of bound sulfur, which may be liberated as the native element or find its way into sulfides, organic matter, or other compounds, sulfates occurring in solution or in sediments contain an appreciable percentage of the earth's oxygen that is readily available for recombination with carbon, hydrogen, or other elements (Redfield, 1958). Sulfates are probably second only to carbonates and carbon dioxide as a reservoir of potentially available oxygen. The fossil oxygen content of sulfates in sea water and sediments is about 50×10^{20} g as compared with a total of 12×10^{20} g of free oxygen in the atmosphere plus that dissolved in the hydrosphere.

The sulfate content of natural waters ranges roughly from less than 5×10^{-5} to 6% in highly saline ponds and lakes (Hutchinson, 1957). In the Dead Sea and Great Salt Lake water contains nearly 2% sulfate. The mean sulfate content of freshwater lakes is in the neighborhood of 0.001%. Sea water of average salinity (3.45% total dissolved solids) contains about 0.265% sulfate (Sverdrup *et al.*, 1942). This is equivalent to 0.0884% sulfur or 28.24 mg-atoms of sulfate sulfur per liter. Thus the total sulfate sulfur content of sea water is about 12×10^{20} g, assuming the volume of all oceans including adjacent seas to be 13.72×10^{8} km^3. The remainder of the hydrosphere, including polar and glacial ice, and ground water plus the water in inland seas, lakes, rivers, and in the atmosphere, is estimated to contain 5×10^{16} g of sulfate sulfur.

Various estimates for the volume of sediments produced during geological time range from 2 to 7×10^{8} km^3. Assuming the volume of such sediments to be 3×10^{8} km^3, their density to be 2.5, and their average sulfur content to be 0.2%, there would be 15×10^{20} g of sulfur in such sediments. Since the majority of the sulfur in sedimentary material is believed to occur as sulfates, it follows that sulfate sulfur occurs in sediments in about the same order of magnitude as the amount dissolved in the hydrosphere. The assumed average sulfur content of sedimentary rocks of

0.2% was approximated from Clarke's (1924) data (see also Mason, 1958, pp. 147 and 181):

Kind of sediment	Relative amount of each sediment	Average sulfur content as SO_3	Average sulfur content as SO_4	Average content of sulfur
		%	%	%
Shale	80	0.64	0.76	0.26
Sandstone	15	0.07	0.08	0.03
Limestone	5	0.05	0.06	0.02

Sulfates, both mineral and organic, are associated with and are modified by living organisms. The total amounts found in body fluids and tissues of organisms, though, are insignificantly small as compared with the vast reservoir of sulfate dissolved in the hydrosphere or occurring in sedimentary materials. Sulfur, taken up by plants primarily as sulfate, occurs in both plants and animals largely in proteins and other carbon compounds. The total sulfur content of living organisms, exclusive of a few algae and sulfur bacteria, ranges roughly from 0.05 to 5%, the exact amount depending upon species and nutritional conditions. This may be compared with a carbon content of approximately 50%. Taking 0.2% sulfur as the average, and using a value of 12×10^{16} g/year as the amount of carbon fixed photosynthetically, there would be 2.4×10^{14} g of sulfur converted into organic compounds annually. At this rate, an amount of sulfate sulfur equivalent to the total content of the hydrosphere would be cycled through organisms in the course of a few million years. This estimate does not take into account the cycling of sulfate through the activities of sulfate-reducing bacteria, which tend to convert sulfate into sulfides or free sulfur in certain anaerobic environments. Sulfur enters the biomass largely in the form of soluble sulfates; it leaves the biomass in the form of sulfates, sulfides, free sulfur, and various organic sulfur compounds. In sulfureta (Baas-Becking, 1925) an atom of sulfur may be cycled through or by organisms numerous times each year.

Because of the cyclic or rapidly reversible nature of the process in the biosphere, there is no good basis for estimating the quantities of sulfate reduced by bacteria. The importance of the process is indicated, though, by the studies of Redfield (1958) who records, "My supposition is that the actual quantities of oxygen present in the sea may have been regulated by the activities of sulfate-reducing bacteria." Such bacteria have the ability to use sulfates as a source of oxygen when free oxygen is absent and organic compounds are present to supply a source of energy. Sulfate reduction followed by the photosynthetic reduction by green plants of the resultant carbon dioxide in the presence of light yields free oxygen:

$$SO_4^{2-} + 2C \rightarrow S^{2-} + 2CO_2$$

$$CO_2 + h\nu \rightarrow 2C + 2O_2.$$

The principal geochemical paths of sulfate in the sea are depicted by Fig. 1.

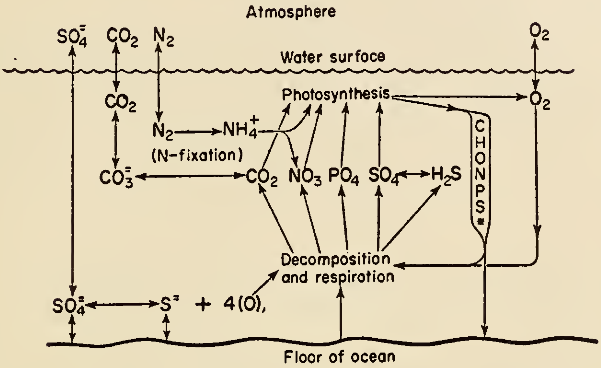


FIG. 1. Principal features of the biochemical cycles in the sea showing some of the interactions of sulfur with other elements. The asterisk (*) indicates elements besides carbon, hydrogen, oxygen, nitrogen, phosphorus and sulfur which make up organic matter.

Sulfur in Soil

In the process of weathering, sulfide in rocks is converted into sulfate in the presence of water and atmospheric oxygen. Rain water adds appreciable quantities of sulfate to soil, particularly near the sea and in the vicinity of industrial areas. In arid regions irrigation water carries sulfate to the soil (Conrad, 1950), although the general tendency is for both irrigation and rain water to leach much more sulfate from the soil than the amounts added. In humid regions sulfate may be largely leached away to rivers and ultimately to the sea. Where evaporation equals or exceeds precipitation, sulfate tends to accumulate in the soil unless removed by agricultural crops. Under arid conditions, sulfate may accumulate and separate out in gypsum deposits.

According to Jordan and Reisenauer (1957), good yields of agricultural crops require an average of from 10 to 50 lb of sulfur per acre per year (*ca.* 1.8 to 9 kg/hectare). In many arable soils, sulfur has to be replenished by the farmer to maintain crop yields. More than one-third of the sulfuric acid manufactured in U.S.A. is consumed by the fertilizer industry (Sauchelli, 1950). Soil sulfur deficiencies are often corrected by the application of gypsum, ammonium sulfate, or potassium sulfate. Certain other soil amendments, fungicides, insecticides, and animal manures supply considerable quantities of sulfur. Superphosphate and various mixed commercial fertilizers, applied to soil primarily for their phosphorus, nitrogen, or potassium content, contain from 0.1 to 20% sulfur (Mehring and Bennett, 1950).

Elemental sulfur is sometimes applied to soil to correct sulfur deficiency or, more commonly, to increase soil acidity. Generally present in well-oxygenated soils are bacteria which oxidize sulfur to sulfuric acid (Starkey, 1950). The continued application of elemental sulfur to soil may result in excessive acidity or gypsum accumulation.

Sulfur is usually absorbed by plants as the sulfate ion (Thomas *et al.*, 1950); some may enter the leaves as sulfur dioxide from the atmosphere. Certain plants appear to utilize cystine, methionine, or elemental sulfur (Thomas, 1958). Sulfur in many soils occurs chiefly in organic compounds. Organic-rich soils in humid regions may contain from 350 to 2100 lb of sulfur per acre-foot (Jordan and Reisenauer, 1957), equivalent to approximately 100 to 600 p.p.m., of which less than 1 p.p.m. may be present as sulfate ion. Thomas *et al.* (1950) record the sulfate content of 11 Western States soils to range from less than 1 p.p.m. to more than 3000 p.p.m.

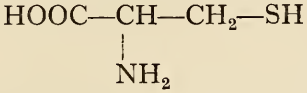
The transformation of organic sulfur into sulfate ion is largely an animal and microbial process. Under certain conditions, though, bacteria and allied microorganisms compete with plants for sulfur to the extent of causing a sulfur deficiency. In the presence of easily decomposable organic matter, soil microbes assimilate sulfate ion, incorporating the sulfur largely in organic compounds as part of their own protoplasm. Sulfur thus bound becomes available to plants only after the death and decomposition of the microbes. Anaerobic conditions, as in organic-rich or water-logged soils, are conducive to the decomposition of organic matter and the reduction of sulfates with the formation of hydrogen sulfide, which is toxic for most plants. Moreover, hydrogen sulfide tends to create reducing conditions or a low redox potential (ZoBell, 1946). By combining with free oxygen, microbially produced hydrogen sulfide is responsible for the depletion of free oxygen in extensive areas in marshes, swamps, rice paddies, and other water-logged soils.

Sulfur in Organisms

All living organisms require sulfur in a suitable form. The sulfur requirements of most photosynthetic plants are satisfied largely by dissolved sulfates, which are converted into constituents of proteins and many other products. Certain autotrophic bacteria oxidize inorganic forms of sulfur (H_2S, S, $S_2O_3^{2-}$, SO_3^{2-}) as their primary source of energy and structural sulfur (Starkey, 1956). The more complex sulfur requirements of animals are met largely by cysteine, cystine, methionine, biotin, and thiamine (Young and Maw, 1958). Cysteine is a component of the tripeptide glutathione and is a precursor of coenzyme *A* and taurine. Methionine is involved in the synthesis of proteins, creatine, and adrenalin.

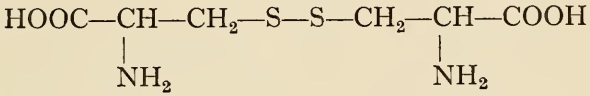
Most proteins contain cysteine, cystine, and methionine. The latter is an indispensable amino acid for all plants and animals that have been studied and for many microorganisms. Animals can convert methionine into cystine, the first step in the conversion being the demethylation of methionine to produce homocysteine (Greenberg, 1954). Neither homocysteine nor cystathione, formed from the conjugation of cystathione with serine, has been found in natural materials. Both appear to be converted metabolically into cysteine and cystine as fast as they are formed *in vitro.* Certain microorganisms metabolize cyst(e)ine with the formation of methionine. Most microorganisms, like green plants, synthesize cysteine and other organic sulfur compounds from sulfate sulfur. Sulfate ions are believed to be reduced by such organisms to sulfite ions, and these in turn are reduced further to sulfide ions, which can then be incorporated into cysteine and transferred to methionine. Cystine is formed by the oxidation and conjugation of two molecules of cysteine.

Cysteine



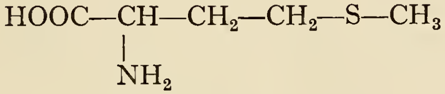
$HOOC{-}\underset{\underset{NH_2}{|}}{CH}{-}CH_2{-}SH$

Cystine



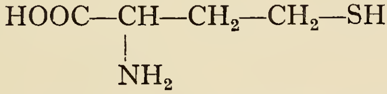
$HOOC{-}\underset{\underset{NH_2}{|}}{CH}{-}CH_2{-}S{-}S{-}CH_2{-}\underset{\underset{NH_2}{|}}{CH}{-}COOH$

Methionine



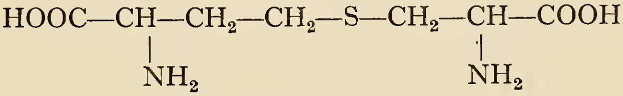
$HOOC{-}\underset{\underset{NH_2}{|}}{CH}{-}CH_2{-}CH_2{-}S{-}CH_3$

Homocysteine



$HOOC{-}\underset{\underset{NH_2}{|}}{CH}{-}CH_2{-}CH_2{-}SH$

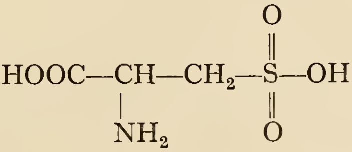
Cystathione



$HOOC{-}\underset{\underset{NH_2}{|}}{CH}{-}CH_2{-}CH_2{-}S{-}CH_2{-}\underset{\underset{NH_2}{|}}{CH}{-}COOH$

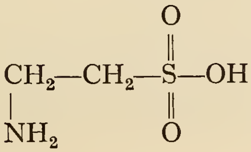
Besides occurring in proteins, cysteine is also a component of the metabolically important glutathione, a tripeptide widely distributed in plant, animal, and microbial cells. Taurine is derived from the metabolism of cysteine and methionine with cysteic acid being an intermediate compound. Taurine occurs in the free state in many invertebrates and as a component of taurocholic acid in the bile of mammals.

Cysteic acid



$HOOC{-}\underset{\underset{NH_2}{|}}{CH}{-}CH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OH$

Taurine



$\underset{\underset{NH_2}{|}}{CH_2}{-}CH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OH$

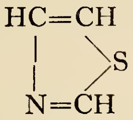
Various organisms also convert cysteine and/or cystine into mercapturic acids, cysteinesulfinic acid, and thiazolidine derivatives, according to Young and Maw (1958). They outline the metabolism of methionine into proteins, homocysteine, adenosylmethione, and methylthioadenosine. Other major sulfur compounds listed by Greenberg (1954) as being important in animals are thiohistidine, mercaptoethaneamine, betaine, ergothionine, thetins, thiocyanates, thiosulfate, and organic as well as inorganic sulfates.

Animals normally excrete amino acid sulfur as sulfates, about 90% being as inorganic salts. Approximately 10% is excreted as phenolsulfuric acid ($C_6H_5—O—SO_3H$), *p*-cresolsulfuric acid ($CH_3—C_6H_4—O—SO_3H$), and indoxylsulfuric acid ($C_6H_4NHCH{:}C—O—SO_3H$). Soil bacteria attack these ethereal sulfates with the liberation of inorganic sulfate or hydrogen sulfide, the end products depending upon bacterial species and environmental conditions.

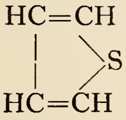
The sulfate content of blood and other body fluids in various animal species ranges from 0.02 to 2%. The bones of most vertebrates contain some calcium sulfate. Up to 0.5% sulfur, present primarily as inorganic sulfate, has been reported (Vinogradov, 1953) in oyster shells; and nearly as much in the skeletons of certain cephalopods and coralline algae. Piscian otoliths generally contain small amounts of calcium sulfate. The occurrence of strontium sulfate in radiolarian skeletal material and of barium sulfate in certain deep-sea rhizopods has also been reported by Vinogradov (1953) in observations which deserve corroboration.

There is a wide range in the sulfur content of living matter as well as in the ratio of organic to inorganic sulfur; variations depend upon conditions, species, the part or tissue of the organism, its age, and conditions of growth or cultivation. Data compiled by Spector (1956) show that the dry weight of certain animals and some plants contains as little as 0.01% sulfur, although most organisms contain from 10 to 100 times as much. The dried cells of a few species of sulfur bacteria contain from 5 to 80% sulfur, however, the sulfur content of most bacteria falls within the range of 0.04 to 8.9% (mostly 0.1 to 1%) of their dry weight. The dry matter in a large number of different seed-bearing plants contained from 0.01 to 1.65% (mostly 0.05 to 0.2%) sulfur (Spector, 1956). The sulfur content of dry plant leaves has been reported by Thomas *et al.* (1950) to range from 0.04 in certain conifers to 3.5% in some salt grasses. Whether organic or inorganic sulfur was the predominant form seemed to be a function of plant species and environmental conditions. As a class, the brown algae (Phaeophyceae) have the highest sulfur content of any organisms except the sulfur bacteria. According to several published analyses compiled by Vinogradov (1953), the dry matter of brown algae contained from 0.65 to 8.97% sulfur. Red algae (Rhodophyceae) have been reported to contain from 0.05 to 3.45% sulfur in the same terms of reference.

Sulfur compounds in plants include the amino acids cystine and methionine, glutatione, several enzymes, two vitamins, sulfates, and numerous organic compounds whose functions have yet to be established. The vitamins biotin and thiamin are thiazole and thiophene derivatives respectively:



Thiazole

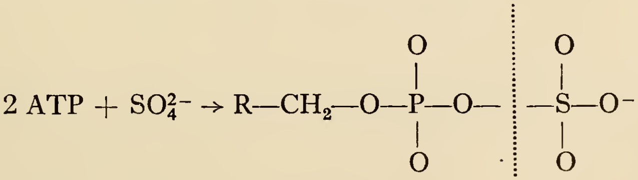


Thiophene

A good many organisms synthesize these vitamins, which are essential for most organisms. Penicillin, synthesized by a fungus, also contains the thiazole ring (Starkey, 1956). The enzyme cocarboxylase is a pyrophosphate of thiamin (Schwarze, 1958). Thomas (1958), who has reviewed this subject, characterizes cytochrome C as an iron enzyme with the thioether linkages between the hematin and protein. Lipoic acid (6,8-thiotic acid) is known to be biologically active, allegedly as a catalyst in photosynthesis. Certain plants contain the glycosides sinalbin and sinigrin as well as their hydrolytic products, although the function of these sulfur compounds has not been determined. The principal constituent of mustard oils is allyl isothiocyanate with lesser quantities of butyl, benzyl, propenyl, and other isothiocyanates. Methyl, allyl, and vinyl sulfides, disulfides, and mercaptans are important constituents of a number of plant families such as the mustards and onions, but are unimportant or absent in other plants. Dithiol isobutyric acid has been found in asparagus (Thomas, 1958).

The occurrence and transformations in plants of thiols, sulfides, sulonium derivatives, sulfoxides, sulfones, and isothiocyanates has been reviewed by Kjaer (1958). He lists as constituents of a few plants dimethyl sulfide, divinyl sulfide, dicrotyl sulfide, diallyl disulfide, allylpropyl disulfide, diallyl trisulfide, methylthiolpropyl alcohol, dimethylthiol propionate, methanethiol, propanethiol, sulforaphene, glucoiberin, glucocheirolin, erysolin, and twenty-seven different glucosides which, upon hydrolysis, yield various isothiocyanates.

Plants absorb and transport sulfur primarily as sulfate ion. The first step in the reduction of sulfate is generally believed to be to sulfite, probably via an organic pathway (Butlin and Postgate, 1956; Thomas, 1958). Lipman's (1958) observations suggest that the initial step in the reduction of sulfate might be its activation by adenosine triphosphate (ATP):



$$2\,\mathrm{ATP} + \mathrm{SO_4^{2-}} \rightarrow \mathrm{R{-}CH_2{-}O{-}}\overset{\displaystyle \mathrm{O}}{\underset{\displaystyle \mathrm{O}}{\mathrm{P}}}\mathrm{{-}O{-}}\ \vdots\ \mathrm{{-}}\overset{\displaystyle \mathrm{O}}{\underset{\displaystyle \mathrm{O}}{\mathrm{S}}}\mathrm{{-}O^-}$$

The second step might then involve breaking the bond at the position indicated by the dotted line. Lipman points out that sulfate is bound, mostly in ester linkage, in a large variety of compounds present in living organisms.

Most important are sulfated mucopolysaccharides, such as chrondroitin sulfuric acid in cartilage and similar mucoitin sulfuric acid in mucosous tissues. Heparin is in this group. A sulfurylated cerebroside is present in brain and other tissues. Conjugation with sulfate is a means of phenol detoxication in the animal body.

More than 95% of the sulfur content of the bacterium *Escherichia coli* was found by Roberts *et al.* (1955) to be present in cysteine, cystine, and methionine. The methionine occurred exclusively in proteins, whereas half of the cyst(e)ine occurred in glutathione. The average sulfur content of dry *E. coli* was 1.12%. The sulfur requirements for the nutrition of this organism were satisfied by sulfate. It also readily utilized sulfite, thiosulfate, cystine, and lanthionine. The sulfate was believed to be reduced successively to sulfite, thiosulfate, and sulfide through a series of organic complexes designated by R:

$$R'SO_4 \rightarrow R''SO_3 \rightarrow R'''S_2O_3 \rightarrow R^nSH$$

The penultimate reaction is believed to involve the incorporation of the reduced sulfur with serine to form cyst(e)ine. Bacteria as well as higher plants metabolize cyst(e)ine with the formation of methionine. For additional information on the metabolic pathways and forms of sulfur in bacteria, plants, and animals the reader is referred to Bersin (1958), Schwarze (1958), Roberts *et al.* (1955), Hanson (1956), Butlin and Postgate (1956), and Dodgson (1956).

Sulfate Reduction

Being very stable, sulfates do not give up their oxygen or set sulfur free in any other form without the expenditure of energy. The reduction of one gram-molecular weight of sulfate to sulfide under standard conditions requires nearly 200,000 cal (Wiame, 1958). Plants, which reduce sulfates to satisfy their sulfur requirements, obtain the necessary energy from solar radiations. Sulfate-reducing bacteria oxidize carbon compounds or molecular hydrogen to obtain energy.

It has been reported that at elevated temperatures and pressures sulfates may combine spontaneously with oxidizable substances such as charcoal or carbon compounds:

$$CaSO_4 + 4C \rightarrow CaS + 4CO$$

According to Behre and Summerbell (1934), sulfates were reduced to sulfides by paraffin-base crude oil samples after a few days at 125°C, but only negative results were obtained at 25°C. Feely and Kulp (1957) detected no sulfide in mixtures of sulfates and petroleum heated for several weeks at 100°C, but they found appreciable quantities of free sulfur resulted from bubbling hydrogen sulfide through sulfate solutions at 50°C:

$$CaSO_4 + 3H_2S \rightarrow 4S + Ca(OH)_2 + 2H_2O$$

Such observations raise many questions regarding the temperature, pressure, kinds of oxidizing agents, and other conditions required for the direct reduction of sulfates and the extent to which such reduction takes place in the weathering of rocks. In soil, recent sediments, and the biosphere, sulfate reduction seems to be largely, if not exclusively, biochemically catalyzed.

Virtually all kinds of plants, including bacteria, absorb sulfate from soil or water to satisfy their sulfur requirements. The absorbed sulfate is probably reduced first to sulfite and then stepwise to the sulfhydryl form (—SH) which is incorporated in cysteine, methionine, and cystine as components of plant proteins. Reduced sulfur also occurs in certain plant hormones, vitamins, and other organic compounds. Animals eat plants or other animals to obtain essential sulfur. During the bacterial decomposition of the organic remains of plants and animals, sulfur is liberated largely as sulfates or hydrogen sulfide. Sulfates predominate under aerobic conditions of decomposition. In the absence of free oxygen, large quantities of hydrogen sulfide are liberated from decomposing proteins (Fig. 1).

Sulfate assimilated by plants, including bacteria, is believed to be a major source of the sulfur content of coal and petroleum. Crude oils contain sulfur in amounts ranging from 0.1 to 5.5% by weight (Levorsen, 1954). It occurs as free sulfur, hydrogen sulfide, mercaptans, disulfides, cycloparaffinic sulfides, thiophenes, thiophanes, and in other forms (see Chapter 7). Much is present in sulfur–hydrocarbon complexes of high molecular weight. While part of the sulfur may be derived from the bodies of plants and animals, perhaps much more results from reactions of hydrocarbons or their derivatives with sulfate, hydrogen sulfide, or sulfoxy compounds resulting from the reduction of sulfate.

Coal, believed to have been formed predominantly from lignin, contains up to 13% sulfur, generally 0.5 to 5% (Breger, 1958). It occurs as metallic sulfides, sulfates, native sulfur, thiols, disulfides, cyclic carbon compounds, and various other complexes. As in petroleum, part of the sulfur was probably derived from decomposed organisms and part from reactions of hydrogen sulfide with coal constituents to yield organic sulfur structures.

Calculated from the sulfur content of the standing crop of marine vegetation as well as from the sulfate uptake of plants growing in soil and in experimental aquaria, plants appear to reduce from 10 to 100 × 10^{13} g of sulfate sulfur per year. Average agricultural crops require from 10 to 40 lb of sulfur per year (Jordan and Reisenauer, 1951); marine vegetation probably consumes much more. Besides the sulfate that plants and bacteria absorb and reduce to satisfy their sulfur requirements, large amounts of sulfate are reduced to sulfides by sulfate-reducing bacteria which utilize sulfate as a hydrogen acceptor.

Sulfate-reducing Bacteria

In the sense that they can assimilate sulfate as a source of sulfur essential for cell synthesis, most bacterial species as well as algae and higher green plants reduce sulfate. It is reduced largely to sulfhydryl components of protoplasm, which ultimately is decomposed with the liberation of some hydrogen sulfide. Only a few specialized bacterial species, however, notably those of the genus *Desulfovibrio*, utilize sulfate directly to oxidize carbon and hydrogen compounds:

$$R{:}CH_2 + CaSO_4 \rightarrow H_2S + CaCO_3 + R{:}O.$$

In this theoretical example, $R{:}CH_2$ represents an organic compound and $R{:}O$ represents oxidation products such as H_2O or CO_2. Virtually all kinds of organic matter, including carbohydrates, lipids, organic acids, and proteins or their hydrolysis products are oxidized in the absence of free oxygen by sulfate-reducing bacteria, working either alone or in association with other anaerobic bacteria. It is a moot question whether hydrocarbons are oxidized directly by pure cultures of sulfate reducers (ZoBell, 1958). Certain varieties, though, oxidize molecular hydrogen:

$$4H_2 + SO_4^{2-} \rightarrow H_2S + 2OH^- + 2H_2O.$$

Molecular hydrogen may come from the fermentation of organic matter (ZoBell, 1947), the radiolysis of organic compounds (Sheppard, 1944), other physiochemical reactions (Nichols, 1941), or from juvenile sources (Clarke, 1924). Being highly mobile, hydrogen could migrate for some distance through the upper crust of the earth. It has been postulated by Heck (1940) that ferrous sulfide may react with hydrogen sulfide in petroliferous sediments to yield hydrogen:

$$FeS + H_2S \rightarrow FeS_2 + H_2.$$

The abundant and widespread occurrence of hydrogen-oxidizing sulfate-reducing bacteria in recent marine and lacustrine deposits, where there is no other source of energy for their growth, is indicative of available hydrogen. Its rapid and quantitative oxidation by sulfate reducers may help to account for the paucity of hydrogen in natural gases.

Perhaps the most important function of sulfate-reducing bacteria in geochemical cycles is in making the fossil oxygen of sulfate available for the oxidation of organic matter (Redfield, 1958). Ordinarily oxygen is required from extraneous sources to provide for the complete oxidation or mineralization of organic matter. Sulfates help to satisfy this biochemical oxygen demand (B.O.D.) of organic matter undergoing decomposition in anaerobic environments such as stagnant water basins and in virtually all recent sediments slightly below the mud–water interface (see Fig. 1). Theoretically, the B.O.D. of 1.0 g of the organic remains of plants and animals of average composition may be satisfied by about 1.5 g of SO_4^{2-}:

$$2(CH_2O) + SO_4^{2-} \rightarrow 2CO_2 + 2OH^- + H_2S.$$

Sulfate-reducing bacteria, which catalyze the reaction, are abundant in marine bottom deposits, soil, sewage, stagnant water basins, and lacustrine sediments. They have been found in sulfur deposits from salt domes and in reservoir fluids and borings from oil wells to depths of several thousand feet. The significance of their presence is conjectural. Various hypotheses link sulfate reducers with the formation of sedimentary sulfur deposits (Hunt, 1915) and with the origin, migration, and modification of oil (ZoBell, 1952).

Ecologically, sulfate-reducing bacteria are very versatile. They tolerate wide extremes of climate (ZoBell, 1958), and various strains have been found in and cultivated in aqueous solutions ranging in salinity from less than from 0.1 to nearly 30%. Most strains grow best or only within the temperature range of 20° to 45°C, although some grow slowly at temperatures as low as 0°C; others grow at temperatures as high as 85°C. When held at a pressure of 1000 atm, one culture grew and reduced sulfates to hydrogen sulfide at 104°C. Although found in natural habitats ranging in reaction from pH 4.5 to 10, most sulfate reducers grow best between pH 6.5 and 8. They are strict anaerobes, growing and reducing sulfates only in the absence of free oxygen. Like all living organisms, they require water and a source of energy. The latter may be provided by organic matter and/or by free hydrogen.

Living sulfate reducers have been taken from the sea floor at stations where water depths exceed 30,000 ft. Such bacteria have been found in oil well brines at depths exceeding 10,000 ft (ZoBell, 1958). Their survival and biochemical activities in sedimentary materials depend upon the following environmental conditions: (a) Interstitial spaces in the sediments must be larger than the bacteria, say 5 or more microns in diameter; (b) Free water must be present with some sulfate in solution; (c) There must be at least traces of phosphate, calcium, magnesium, potassium, iron, chloride, and nitrogen in an available form to provide for cell development—ammonia satisfies the nitrogen requirements of most sulfate reducers; a few fix nitrogen (Sisler and ZoBell, 1951); (d) Either oxidizable carbon compounds or free hydrogen must be present to supply energy; (e) Reducing conditions are prerequisite; (f) Toxic substances must not be present in bacteriostatic concentrations. Many heavy metals such as nickel, copper, zinc, and mercury are toxic as are certain metabolic products of the bacteria themselves. Sulfate reducers are unique, though, in their tolerance of high concentrations of hydrogen sulfide and of the constituents of most crude oils. (g) Temperatures above 85°C are generally limiting, except at great depths, where hydrostatic pressures increase the temperature tolerance of bacteria.

In the process of the reduction of sulfate to hydrogen sulfide the sulfur must pass through several intermediate forms, but there is direct evidence only for traces of sulfite (Postgate, 1951). Facts and recent theories regarding intermediates in sulfate reduction are treated by Roberts *et al.* (1955), Postgate (1958), Thomas (1958), Wiame (1958), Young and Maw (1958), and by Ishimoto and Fujimoto (1959).

Occurrence and Formation of Hydrogen Sulfide

Besides the hydrogen sulfide resulting from sulfate reduction and that emanating from volcanoes, fumaroles, solfotaras, and hot springs, appreciable quantities arise from the weathering of metallic sulfides and from the decomposition of proteinaceous materials. Hydrogen sulfide is a common though minor constituent of volcanic gases (Zies, 1938; Rubey, 1951). The concentration range is from nil to 20%, but generally less than 0.1%. Although present in very small percentages, the total amounts evolved are enormous. Based upon variously reported analyses, it is estimated that 2–5 × 10^{12} g of hydrogen sulfide has emanated annually from volcanoes and fumaroles in recent years. This hydrogen sulfide, like that which escapes into the atmosphere from other sources, is rapidly rained back to earth or undergoes spontaneous oxidation in moist air. Being chemically reactive and more dense than air, little or no hydrogen sulfide occurs in the upper atmosphere. In the presence of sunlight and oxygen, hydrogen sulfide is photochemically oxidized to sulfur dioxide (Jacobson and Hampel, 1958):

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

Volcanic emanations excepted, natural gases rarely contain appreciable quantities of hydrogen sulfide. There is little or none in most petroleum gases, although a few oil fields produce gases containing from 0.1 to 5% or more hydrogen sulfide by volume (Ley, 1935). As examples of exceptional conditions, Levorsen (1954) describes natural gases from an Iranian oil field and one from a northeastern Texas field having hydrogen sulfide contents of 40 and 42.4% respectively. Traces of mercaptans, notably CH_3SH and C_2H_5SH, have been found in a few natural gases. Mercaptans could result from reactions between sulfur or hydrogen sulfide and certain carbon compounds at relatively high temperatures and pressures, but decomposing protein is a more probable source. Hydrogen sulfide may find its way into natural gases from decomposing protein, sulfate reduction, or from the reaction of mineral acids on metallic sulfides:

$$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S$$

Conditions necessary for the latter reaction may be realized mainly in magmatic formations; rarely if ever in sedimentary deposits. Sulfate reduction by bacteria seems to be the most likely source of hydrogen sulfide in natural gases of sedimentary origin.

Up to 20% by volume of the gas recovered from numerous samples of meteorites, volcanic rocks, and granite consists of hydrogen sulfide along with variable quantities of carbon dioxide, methane, nitrogen, and hydrogen (Clarke, 1924). In many cases, though, it is questionable as to how much of each gas was indigenous and how much may have resulted from treatment of the rock samples with heat, water, or other agents to expel occluded gases during analytical operations.

Hydrogen sulfide is a common though very minor constituent of marsh gas. Large amounts are produced in marshes, swamps, soil, and putrefying materials, and much escapes into the atmosphere.

Relatively little hydrogen sulfide occurs in the hydrosphere due partly to its incompatibility with dissolved oxygen and other oxidizing agents. It is present in many ground waters, rarely in unpolluted rivers, mostly only at the bottoms of lakes, and in the sea only under exceptional conditions; e.g. stagnant water basins, contaminated nearshore water, and occasionally in the wake of plankton blooms. Bottom water in stagnant Norwegian fjords and in the Black Sea contains hydrogen sulfide in concentrations up to 14 mg/l. (Sverdrup *et al.*, 1942). Although conventionally designated "hydrogen sulfide", because it may react as such, ordinarily only a part of it occurs in water as free or dissolved hydrogen sulfide; part of it is present as bisulfide or the sulfide of some base, e.g. sodium bisulfite or sodium sulfide. Sulfide is not found in the topmost 100 m of water in the Black Sea; below this depth it increases in concentration from 1 mg/l. at 200 m to 14 mg/l. at depths of 800 m or more. Contaminated bays and other inshore or nearshore waters may contain hydrogen sulfide in concentrations up to 10 mg/l. at the bottom. Traces of hydrogen sulfide may be present at the surface. In fact, hydrogen sulfide sometimes escapes from water into the atmosphere as indicated by its odor and its blackening of white lead-base paints.

According to Hutchinson (1957), the bottom waters of many oxygen-deficient lakes contain hydrogen sulfide in concentrations ranging from traces to 45 mg/l. An extreme case is 786 mg/l. reported for Big Soda Lake in Nevada, this undoubtedly being total sulfide in solution. Interstitial water in highly reducing lacustrine and recent marine sediments may be saturated with hydrogen sulfide. It is a common constituent of oil field waters in which concentrations up to 2400 mg/l. have been reported (Ginter, 1934). Bacterial sulfate reduction is believed by many workers to be the chief source of hydrogen sulfide in oil well or formation waters.

The microbial decomposition of the organic remains of plants and animals results in the liberation of hydrogen sulfide. Numerous species of bacteria participate in the process. In the absence of free oxygen, bacteria convert organic sulfur almost quantitatively into hydrogen sulfide. Traces of mercaptans may be produced (Bunker, 1936). Hydrogen sulfide produced in excess of the equivalent sulfur content of organic compounds results from sulfate reduction by bacteria that obtain their energy from the oxidation of organic matter. From her own observations and documented work of others, Clarke (1953) shows that most species of bacteria liberate hydrogen sulfide from cysteine. Less common are bacteria which form hydrogen sulfide from cystine, thiosulfate, or sulfate.

Little is known regarding the formation of hydrogen sulfide in higher plants. Small amounts are produced enzymatically in animals from the intermediate metabolism of cyst(e)ine and methionine (Hanson, 1956). That produced in the gut of animals is attributed primarily to the activities of putrefying bacteria.

By virtue of its toxicity for most plants and animals and its competition for free oxygen, hydrogen sulfide is an important ecological and biogeochemical agent over extensive areas of the earth. Hydrogen sulfide is responsible for anaerobic conditions in stagnant water basins, swamps, marshes, polluted waters, and elsewhere in the biosphere. In such places, it restricts the growth or occurrence of biota and influences oxidation states of many substances (ZoBell, 1946). In the Black Sea, hydrogen sulfide, produced by putrefying and especially by sulfate-reducing bacteria in deeper water strata, quantitatively reacts with atmospheric and photosynthetically produced oxygen from shallow layers, thereby rendering conditions anaerobic and almost lifeless. Several observers have referred to a milky or turbid layer of water caused by the occurrence of colloidal sulfur and sulfur bacteria where oxygen from above converges with hydrogen sulfide from deeper waters.

Sulfides of Iron

In aqueous solution, hydrogen sulfide is ionized in two steps:

$$H_2S \rightleftarrows H^+ + HS^- \rightleftarrows 2H^+ + S^{2-}.$$

The sulfide ions may be oxidized to free sulfur by ferric iron ions:

$$Fe^{3+} + S^{2-} \rightarrow S + Fe^{2+}.$$

Ferrous iron ions react with sulfide ions to yield ferrous sulfide:

$$Fe^{2+} + S^{2-} \rightarrow FeS \text{ (troilite)}.$$

Under certain conditions, which are not well defined and which may be partly biochemically induced, ferrous sulfide reacts with sulfide to give ferroferric sulfide (Fe_3S_4), ferric sulfide (Fe_2S_3), or iron disulfide (FeS_2). The latter occurs in nature as pyrite and as marcasite, both of which are of considerable geochemical significance.

Hydrated ferrous sulfide or hydrotroilite ($FeS.nH_2O$) is a common constituent of reducing sediments (Galliher, 1933). Such sediments generally have a high organic content (1–5%) and from 0.1 to nearly 1% total sulfur occurring mostly in sulfates and sulfides. Copenhagen (1934) reported the presence of from 0.25 to 0.65% sulfur in samples collected from the extensive deposits of black mud in Walvis Bay off the west coast of South Africa. Much of the sulfur was believed to be present as ferrous sulfide, probably hydrotroilite. Such black muds become grey upon exposure to air, ostensibly owing to the oxidation of ferrous sulfide with the formation of elemental sulfur and sulfate. Ferrous sulfide is also a constituent of blue muds which cover extensive areas of the sea floor. Clarke (1924) records an average of 0.13% sulfur in blue and green muds, as compared with up to 7.29% in samples of shale from Colorado.

Pyrite and marcasite are quantatively the most important of a number of sulfides which serve as geochemical indicators in sediments according to Keith and Degens (1959). They point out that frequently there may be a genetic connection between the sedimentary sulfides and organic material. Whether derived from the decomposition of proteins or from the reduction of sulfates, the amount of sulfides produced seems to be primarily a function of the availability of organic matter to serve as a source of hydrogen sulfide or energy for sulfate-reducing bacteria. When sulfates are in good supply, as in marine environments, ordinarily much more hydrogen sulfide is produced from sulfates than from proteinaceous materials. For this reason, ordinarily more sulfides are precipitated, ostensibly as hydrotroilite, in marine environments, where sulfate is abundant, than in fresh water basins. In support of this generalization, Keith and Degens (1959) report the presence of from two to ten times as much sulfide in marine as in fresh water sedimentary deposits. The ferrous sulfide is believed to be formed mostly in the sediments or at the mud–water interface, this being where ferrous iron and hydrogen sulfide are usually most abundant.

At low oxygen tensions, in reducing environments, and apparently in certain organisms, ferrous sulfide may be converted into relatively insoluble iron disulfide (FeS_2) in the form of pyrite with lesser quantities of marcasite and melnikovite. Pyrite has been detected in many sediments from the floor of the ocean in amounts ranging from 0.01 to 0.5%. The content generally increases with depth, age, and degree of reduction of recent marine sediments. Pyrite and occasionally some marcasite were observed in Black Sea muds by Arkhangelsky (1934). He reported finding from 0.3 to 3% pyrite in the passages of certain sponge spicules and foraminifera. Goldschmidt (1954) cites Berz as believing that the transformation of ferrous sulfide into pyrite is accompanied by the formation of magnetite (Fe_3O_4). Woodland (1938) reported the separation of magnetite and siderite ($FeCO_3$) in the conversion of hydrotroilite to pyrite.

Pyrite occurs in rocks of all ages and types, being most abundant in older sedimentary and metamorphic rocks as well as in fossils. Pyrite is a minor constituent of igneous rocks, often being intermixed with other metallic sulfides. Pyrite is found in lignite, coal, certain clays, shales, and limestones in variable quantities particularly in the form of veins, layers, lenses, concretions, or dispersed crystals. Many fossils are mineralized with pyrite, evidently formed by the replacement of organic matter by iron disulfide.

Pyrite originates in various ways. Some has had a contemporaneous origin; other deposits are epigenic. From field observations and laboratory experiments, it is apparent that many deposits of pyrite in organic-rich sedimentary material are of organic origin. Pyrite has appeared in cultures of different kinds of hydrogen sulfide producing bacteria growing in nutrient media containing soluble iron salts. Ferrous sulfide is produced in such cultures:

$$H_2S + FeCO_3 \rightarrow FeS + H_2CO_3$$

Crystalline inclusions inside certain bacterial cells were identified as pyrite by Issatschenko (1929), who believed they resulted from the reaction:

$$FeS + H_2S + \tfrac{1}{2}O_2 \rightarrow FeS_2 + H_2O.$$

Following the death of the bacteria, small crystals of pyrite were liberated. Pyrite found in strictly anaerobic cultures of sulfate-reducing bacteria was believed to result from coupled reactions:

$$FeS + H_2S \rightarrow FeS_2 + H_2 - 2770 \text{ cal} \qquad (1)$$

$$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O + 73{,}130 \text{ cal} \qquad (2)$$

Although the first reaction is endothermic, the simultaneous oxidation of the resultant hydrogen in the second reaction could provide ample energy to make the coupled reactions go. The removal of hydrogen, the insolubility of FeS_2, and the relatively high partial pressure of H_2S are all equilibrium conditions which tend to drive the first reaction to the right.

Another hypothetical exothermic reaction involves sulfite, which is generally believed to be an intermediate product in the reduction of sulfate:

$$2FeS + 2H_2S + H_2SO_3 \rightarrow 2FeS_2 + 3H_2O + S$$

This reaction, coupled with the oxidation of hydrogen as an energy source for sulfate-reducing bacteria, could account for localized concentrations of pyrite, as in pyritized fossils, in the biosphere. By diffusion or by water movements, all of the necessary reactants could be conveyed to the place where pyritization is taking place. Beyond the biosphere, sulfur from alkaline sulfides is probably transferred to ferrous sulfide at relatively high temperatures and pressures or by the combination of molten sulfur with iron in magma. Many pyrite lenses in schists and other metamorphic rocks appear to be related to igneous intrusions.

Under certain conditions of partial pressure at temperatures exceeding 500°C, pyrite decomposes with the formation of pyrrhotite (Kullerud, 1959). Similarly, at high temperatures covellite (CuS) gives rise to some digenite (Cu_9S_5). Because of the effect of temperature upon the stability of these and other iron and copper sulfides in certain ore bodies, their presence serves as a basis for estimating temperature histories. According to Kullerud (1959), "Information obtained from synthetic sulfide systems, when properly applied, can lead to reliable inferences about conditions existing during the formation of sulfide ores. It is possible, by various means, to estimate not only the temperature relations in ore bodies but also the partial pressure of sulfur." Pyrrhotite does not occur ordinarily in sedimentary formations; it appears to be primarily a product of hot magmatic solutions of iron and sulfur.

Formation and Oxidation of Free Sulfur

Besides the juvenile and secondary sulfur deposited around volcanoes, elemental sulfur occurs extensively elsewhere in nature. Under certain conditions, pyrite and other metallic sulfides may be oxidized during weathering processes with the liberation of some elemental sulfur, although sulfate is the major oxidation product. More commonly, sulfur is formed from the incomplete oxidation of hydrogen sulfide or from the reduction of certain sulfoxy compounds. Such reactions take place either spontaneously or biochemically in the presence of appropriate oxidizing or reducing agents. In bodies of semi-stagnant water, colloidal sulfur may be formed in sufficient amounts to impart a milky or cloudy appearance in strata where hydrogen sulfide diffusing up from anaerobic environments comes into contact with dissolved oxygen.

Bacteria and allied microbes contribute substantially to the formation, occurrence, and oxidation of sulfur throughout the biosphere. Elemental sulfur is a common though very minor constituent of most organic reduced muds and of many sediments. Microbial processes play a major part in its formation. There is less certainty concerning the role of microbial processes in the formation of the massive sedimentary deposits of sulfur in Sicily, Russia, Mexico, Louisiana, Texas, and elsewhere in the world.

Elemental sulfur is formed by several kinds of bacteria. Among the many that form sulfur indirectly are those that produce hydrogen sulfide, which may then be oxidized spontaneously to yield sulfur. *Beggiatoa* species are representative of bacteria which form sulfur directly by oxidizing hydrogen sulfide:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

Ordinarily *Beggiatoa* species oxidize hydrogen sulfide to sulfate, accumulating sulfur as globules in their cells when hydrogen sulfide is in good supply. Under optimal conditions *Beggiatoa* species may oxidize three or four times their own cell weight in hydrogen sulfide daily. Such bacteria are widely distributed in both fresh water and marine environments containing hydrogen sulfide. They are particularly abundant in sulfur springs, pools, swamps, marshes, decaying vegetable matter, and in muds. In many bodies of water such bacteria reproduce rapidly in the zone where hydrogen sulfide produced below mingles with oxygen from above. Some of the bacteria tend to settle into the anaerobic depths where they are unable to oxidize their intracellular sulfur. There are several other genera of bacteria which oxidize sulfide to sulfate with the formation of elemental sulfur globules either intracellularly or extracellularly. These include species of *Thiothrix*, *Thioploca*, *Thiospirillopsis*, *Achromatium*, *Macromonas*, *Thiovolum*, *Thiospira*, and *Thiobacterium* (Starkey, 1956; Schwartz, 1958).

All of the above genera of sulfur bacteria are aerobic. They are not light-dependent or photosynthetic as are several genera of so-called purple and green sulfur bacteria belonging to families Thiorhodacae and Chlorobacteraceae which possess chlorophyllous pigments. These pigmented sulfur bacteria develop photosynthetically in the presence of light, carbon dioxide, and hydrogen sulfide, forming elemental sulfur either intracellularly or extracellularly:

$$CO_2 + 2H_2S + h\nu \rightarrow (CH_2O) + H_2O + 2S$$

where (CH_2O) represents a component of organic matter in the bacterial cell. These photosynthetic bacteria are active in the absence of free oxygen. They occur in shallow waters, sulfur springs, and in shallow bottom material from which hydrogen sulfide emerges.

Thiobacillus thioparus, commonly found in soil, shallow waters, and certain marine sediments, oxidizes thiosulfate and deposits sulfur granules intracellularly:

$$2Na_2S_2O_3 + O_2 \rightarrow 2Na_2SO_4 + 2S$$

Whether hydrogen sulfide-oxidizing species of *Thiobacillus* form sulfur has not been established. Most *Thiobacillus* species are better known for their ability to oxidize elemental sulfur.

Especially remarkable is *Th. thiooxidans*, cultures of which have been known to produce sulfate from the oxidation of sulfur until the reaction of the medium was reduced to pH 1.0 or lower (Starkey, 1956):

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

Th. thiooxidans is most active in acidic media and grows poorly above pH 6.0. It is found in natural environments where acidic conditions have been produced by the oxidation of sulfur. A most remarkable case is Lake Kata-numa, Japan, the waters of which contain 474 mg sulfate per liter and have a pH value of 1.4 (Hutchinson, 1957). *Th. ferrooxidans* is another acid-tolerant bacterium which is unique in being able to oxidize both thiosulfate and ferrous iron (Colmer *et al.*, 1950):

$$Na_2S_2O_3 + 2O_2 + H_2O \rightarrow Na_2SO_4 + H_2SO_4$$

$$12FeSO_4 + 3O_2 + 6H_2O \rightarrow 4Fe_2(SO_4)_3 + 4Fe(OH)_3$$

Th. ferrooxidans was isolated from acid drainage water of coal mines.

Thiobacillus denitrificans oxidizes sulfur either in the presence of oxygen or anaerobically in the presence of nitrate:

$$5S + 6KNO_3 + 2H_2O \rightarrow 3K_2SO_4 + 2H_2SO_4 + 3N_2$$

The mechanism by which elemental sulfur gains entrance into the microbial cell to be assimilated remains obscure. Diffusion in aqueous media seems unlikely in view of the low solubility of sulfur in water. Its transport through fats and oils, in which sulfur is soluble, has been postulated but questioned. Another possibility is its extracellular reduction followed by the transport of the active sulfide into the cell:

$$S^* + 2GSH \rightarrow S^{2-} + GS\text{—}SG + 2H^+$$

where GSH represents reduced glutathione or some similar sulfhydryl compound (see Chapter 10). The sulfide ion, either free or in bound form, can enter the cell in which the chemical reaction may be reversed or the subsequent oxidation of the sulfur to sulfate may yield electrons to reduce GS—SG to 2GSH. Vishniac and Santer (1957) envision the intracellular oxidation of sulfur first to thiosulfate and then successively through steps as follows to sulfate:

$$S^* \rightarrow S_2O_3^{2-} \rightarrow S_4O_6^{2-} \rightarrow S_3O_6^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$$

Both thiosulfate and tetrathionate oxidation appear to be phosphate dependant, possibly through involvement of a mixed anhydride of the type $\text{—S—O—}PO_3^{2-}$. Credence is lent to this hypothesis by the occurrence in protoplasm of phosphoryl sulfate.

Because of the fundamental and geochemical significance of the reaction, the concept that high-energy phosphate bonds are energy-coupling between sulfur oxidation and carbon dioxide assimilation by thiobacilli has received considerable attention. These and related autotrophic sulfur bacteria, which grow in purely mineral solutions, may play an even more important role in nature as synthesizers of organic matter than as modifiers of sulfur.

Sulfate-reducing bacteria of the genus *Desulfovibrio* have been credited with the ability to oxidize elemental sulfur to a limited extent under exceptional conditions (Postgate, 1951). In nature, though, sulfate reducers are far more important as producers than as oxidizers of elemental sulfur either directly or indirectly. Ordinarily sulfates are reduced almost quantitatively to hydrogen sulfide by laboratory cultures of *Desulfovibrio.* While there may be environmental conditions and bacterial species which result in the direct reduction of sulfates to sulfur, as reported by Datta (1946) and Subba Roa (1950), it is generally believed that hydrogen sulfide formed by sulfate reducers is involved in the formation of sulfur. Free or dissolved oxygen could contribute to the process in many places. In anaerobic environments deep in sediments where large amounts of sulfur are formed, other oxidizing agents may be responsible. It has been suggested that either sulfate itself (Feely and Kulp, 1957) or products intermediate in the reduction of sulfates, such as sulfite, may react with hydrogen sulfide as follows:

$$H_2SO_3 + 2H_2S \rightarrow 3H_2O + 3S$$

Be this as it may, it is generally believed that the massive deposits of sulfur associated with cap rock in salt domes (Taylor, 1938) have resulted from the reduction of calcium sulfate. The replacement of the latter with sulfur and calcium carbonate suggests the oxidation of carbon compounds either directly or biochemically. Whether the chemical reactions take place spontaneously is open to question, considering the relatively high temperatures believed to be necessary. Bacteria could catalyze the reactions and account for what is found. The occurrence of sulfate-reducing bacteria deep in sulfur-bearing formations (Miller, 1949; ZoBell, 1958) and the fractionation of stable isotopes of sulfur by sulfate reducers support the bacterial hypothesis for the origin of sedimentary sulfur.

Hydrogen sulfide produced by laboratory cultures of sulfate-reducing bacteria was found (Jones and Starkey, 1957) to be enriched with sulfur-32, the S^{32}/S^{34} ratios of the sulfide being up to 2.7% higher than in the parent sulfate. The S^{32}/S^{34} ratios of elemental sulfur from salt domes were intermediate between the ratios for sulfate and hydrogen sulfide produced from it, indicating that the sulfur may have resulted from a reaction between sulfate and hydrogen sulfide (Feely and Kulp, 1957). According to Macnamara and Thode (1951), the ratios of S^{32}/S^{34} in elemental sulfur were 3.1% higher than in the sulfate from which it was believed to have been formed by microbial processes. The reduction of sulfate by *Desulfovibrio desulfuricans* resulted in a 1.2% depletion of S^{34} in the hydrogen sulfide produced in the laboratory. The S^{32}/S^{34} ratios of several sulfur deposits of biochemical origin ranged from 22.29 to 22.71 as compared with ratios of 21.81 to 22.07 in volcanic deposits.

Isotopes of Sulfur

There are seven isotopes of sulfur ranging in mass from 31 to 37 inclusive. The four stable or nonradiogenic isotopes have average abundances in sulfur from terrestrial sources as follows:

Mass 32	95.018%
Mass 33	0.750%
Mass 34	4.215%
Mass 36	0.017%

There is some variation in the isotopic constitution of sulfur depending upon the source and history of the material. In the limited number of samples analyzed—less than a hundred—the maximum variation in isotopic variations ranged from 2.5% in S^{32}/S^{33} to 10% in S^{32}/S^{36} (Thode *et al.*, 1949). The maximum variation in the more commonly determined S^{32}/S^{34} ratio was about 5% ,the values ranging from 21.58 to 22.70 ± 0.01. The S^{32}/S^{34} ratios of sulfur from several different sources, as recorded by Ault (1959), Thode *et al.* (1949), Ingerson (1953), and Rankama (1952), are summarized in Table 2.

Finding the isotopic content of meteoritic sulfur to be nearly the same as that found in igneous rocks suggested to Macnamara and Thode (1950) that meteorites and the earth had a common origin and that the isotopic content of juvenile sulfur has remained essentially unchanged. Whether the constitution of sulfur in the deeper parts of the earth or in meteorites has remained constant throughout the geological ages seems problematical, but there is ample theoretical and experimental evidence for the fractionation of sulfur in the biosphere. According to Thode *et al.* (1949), the isotopic constitution of sulfur in pyrite appears to be independent of geological age and there is little correlation between the presumed temperature of its formation and its isotopic constitution. The low S^{32}/S^{34} ratio (21.61) found for one sample of pyrite may be due to high temperature of formation or it may mean that the pyrite was derived from sulfate. With the exception of this one sample, all other pyrites had S^{32}/S^{34} ratios ranging from 22.00 to 22.46, compared with from 21.58 to 22.12 for sulfates.

TABLE 2

Ratios of Sulfur Isotopes in Various Materials as reported by Different Investigators

Number of samples	Description and source of material	Ratios of S^{32}/S^{34}	
		Range	Average
14	Troilite phase of meteorites	21.93–22·24	22.15
27	Sulfides from igneous rocks	20.08–22·21	22.13
20	Other samples of pyrite	21.51–22·46	22.16
74	Sulfides in sedimentary rocks	21.28–23·20	22.49
10	Native sulfur of volcanic origin	21.81–22·30	22.07
12	Native sulfur from other sources	21.89–22·70	22.28
7	Rock sulfates (gypsum and anhydrite)	20.84–22·12	21.87
24	Sulfate in sea water	21.70–21·80	21.76
4	Sulfate in well water	21.58–21·73	21.67
6	Hydrogen sulfide in mineral water	22.18–22·79	22.40
10	Organic sulfur compounds	22.12–22·35	22.24

Fractionation is made possible by differences in the chemical properties of the molecules composed of different isotopes resulting in different reaction rates. In general, the molecule containing the lighter isotope reacts faster (Tudge and Thode, 1950). For example, in the exchange reaction

$$S^{32}O_4^{2-} + H_2S^{34} \rightleftarrows S^{34}O_4^{2-} + H_2S^{32}$$

where K, the reaction constant, is 1.075 at 25°C, there is a tendency for sulfur-34 to concentrate in the sulfate, whereas in the exchange reaction

$$H_2S^{34} + S^{32} \leftrightarrows H_2S^{32} + S^{34}$$

where K is 1.000, there should be no change in concentration of isotopes. Bacteria, and probably other organisms which metabolize sulfur, may select isotopes or supply energy for certain fractionation reactions.

Although there is a fairly wide spread in the S^{32}/S^{34} values for each category of samples, secondary sulfates are generally richer in sulfur-34; biogenic sulfur and sulfides are poorer in sulfur-34 than juvenile sulfur.

The elemental sulfur from Cyrenaican lakes in North Africa was found to have an S^{32}/S^{34} ratio of 22.57 as compared with 21.88 for sulfate. Butlin and Postgate (1953) have demonstrated that the sulfur deposited in these lakes results primarily from the bacterial reduction of sulfates. The extent to which spontaneous or microbial oxidation of hydrogen sulfide, a product of sulfate reduction, contributes to the deposition of sulfur has not been established.

Conditions observed in the Cyrenaican lakes and similar environments not only illustrate the depletion of sulfur-34 during the biochemical formation of elemental sulfur from sulfate, but they also illustrate why there are often variations in the isotopic constitution of sulfur within categories of samples. In such environments, termed sulfureta by Baas-Becking (1925), any given sulfur atom may have been in any number of different molecules —sulfides, organic compounds, sulfates, sulfites, thiosulfates, etc., numerous times before being subjected to mass spectrometric analysis.

In preliminary experiments, Kaplan and Rafter (1958) observed small and probably insignificant enrichment of sulfur-34 (-0.05 to $+0.16\%$) by *Thiobacillus concretivorus* during the oxidation of elemental sulfur to sulfate. However, the oxidation of hydrogen sulfide by this organism resulted in a small enrichment of S^{32} (0.6 to $0.9 \pm 0.1\%$) in the sulfate as indicated by increased S^{32}/S^{34} ratios.

Among the natural radionuclides of interest is sulfur-35, with a half-life of 87 days, which is believed to result from cosmic ray interactions. Little is known regarding naturally occurring sulfur-35 in biological systems, but pile produced sulfur-35 is a useful tool for following metabolic pathways (Thomas, 1958). The short life of sulfur-31 and sulfur-37 (2.6 sec and 5.04 min, respectively) make these radionuclides rather uninteresting either in natural materials or in biochemical experiments.

Transportation of Sulfur

Figure 2 outlines some of the major pathways of sulfur as it passes from magma and igneous rocks into the atmosphere, hydrosphere, and biosphere. Although the sulfur content of the atmosphere is almost negligibly small, except near the earth's surface, appreciable amounts circulate in the air, mostly as sulfate with lesser quantities of sulfite, hydrogen sulfide, sulfur dioxide, sulfur trioxide, mercaptans, and organic sulfur.

The sulfur content of atmospheric precipitation ranges from nil to 20 mg/l. the concentration depending upon the amount of precipitation and atmospheric sulfur pollution in the area. Some of the highest values occur in localized industrial areas. Based upon data compiled from various published sources, Rupp (1956) estimates the total sulfur volatilized by the combustion of coal, petroleum, and gas to be about 8 million short tons (72×10^{11} g) per year in U.S.A. Another million tons (9×10^{11} g) per year is volatilized in this country by industries making or using raw sulfur or sulfuric acid, and nearly half a million tons escapes from sulfide ores during smelting. Most of the industrially volatilized sulfur is probably rained down relatively near the place of its generation, its distribution being influenced primarily by precipitation and wind velocities.

Eriksson (1952) has compiled data which indicate that atmospheric precipitation deposits on continental U.S.A. sulfur in amounts ranging from 3 to 260 kg/hectare per year, the mean for rural areas being about 10 kg/hectare per year or 0.1 mg/cm^2 per year. He believes that a great part of the sulfur in precipitation is of oceanic origin, being brought into the air either as spray or as hydrogen sulfide formed by sulfate reduction in the sea, as suggested by Conway (1942). Hydrogen sulfide is also emitted from decaying organic matter and by sulfate-reducing bacteria. Some sulfur enters the air from forest and grass fires and as dust from the Earth's surface and in volcanic emanations. Although sea water spray contributes substantially to the sulfur content of the atmosphere, particularly in coastal areas, other important sources are indicated by chlorine:sulfur ratios of atmospheric precipitation ranging from 0.2 to 20 as compared with 21.5 for sea water.

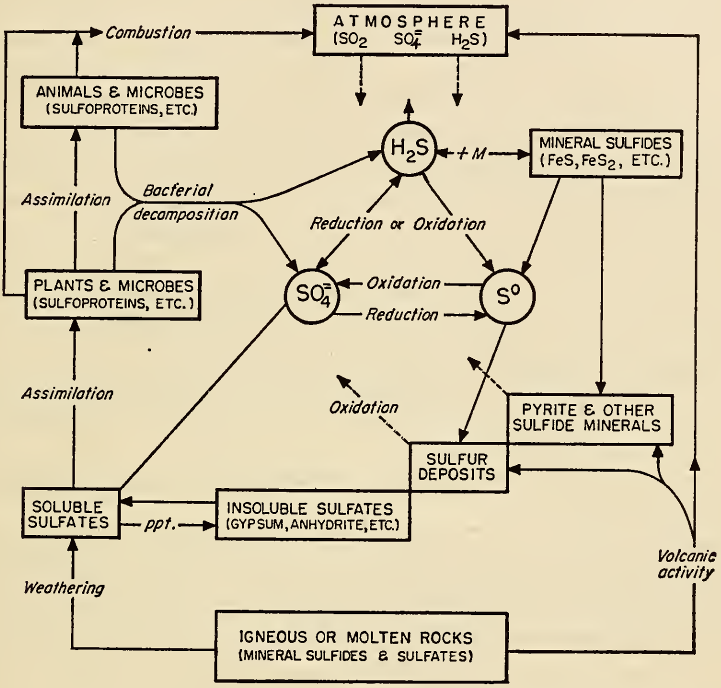


FIG. 2. Cycle of sulfur from primeval earth through the biosphere in sediments, soil, water, and air.

Throughout the geological ages, volcanic emanations may have been a major source of sulfur for sea water and sediments. Sulfur is much too abundant in sea water and marine sediments to be explained as a product of igneous rock weathering alone. Based on the assumption of Goldschmidt

(1937) that 600 g of primary rocks (containing an average of 0.312 g of sulfur) have been weathered for each kilogram of sea water (sulfur content 0.884 g), the transfer percentage or enrichment of sea water with sulfur is 283, or nearly three times the amount supplied by the weathering of primary rocks. Rubey (1951) estimates the total sulfur content of the present hydrosphere, biosphere, and atmosphere to be 13×10^{20} g, plus 15×10^{20} g in ancient sedimentary rocks for a total of 28×10^{20} g, of which only 6×10^{20} g can be accounted for by the weathering of igneous rocks. The "excess" of 22×10^{20} g is attributed to volatile forms of sulfur supplied by volcanic gases and hot springs.

Inland and circulating ground waters constitute only a small percentage (*ca.* 0.02%) of the hydrosphere. Yet these terrestrial waters are of tremendous importance in the weathering, chemical modification, and transportation of sulfur-bearing materials. From Clarke's (1924) data on the discharge volume and sulfur content (mostly in the form of sulfate) of the principal rivers of the world, it is calculated that annually they carry into the sea about 15×10^{13} g of sulfur, or an amount equivalent to 0.14 mg/cm^2 from the 40 million square-mile drainage area. Taking Hutchinson's (1954) estimate of 20×10^{15} liters as the total annual terrestrial runoff and its average sulfur content as 20 mg/l., it follows that annually the sea receives 40×10^{13} g of sulfur (mostly as sulfate) from rivers, ground waters, and other land drainage. Substantially less than half of the sulfur content of terrestrial waters comes directly from the weathering of igneous and metamorphic rocks, according to Conway (1942), who believes that the majority comes from the weathering of sedimentary materials and atmospheric precipitation.

Although living organisms affect the forms of sulfur in water, soil, and sediments and are largely responsible for the parts of the sulfur cycle depicted in the center and upper left-hand corner of Figure 2, they play a very minor role in the world-wide transportation of sulfur or its compounds. Sulfur in most forms is transported mainly by water and air movements. The total amount of sulfur in the bodies of organisms or their organic remains is insignificantly small as compared with the vast reservoir of inorganic forms of sulfur occurring in the hydrosphere and biosphere. The mass migration of terrestrial or aquatic animals accounts for the transportation of only a small fraction of the amount of sulfur in various forms carried by air and water movements. As a geochemical agent, man (by burning sulfur-bearing materials, by shipping sulfur or its compounds, by altering conditions in nature as by water pollution, etc.) has contributed only slightly, except in highly localized areas, to either the cycle of sulfur or its transportation.

Some More Microbial Aspects

Bacteria, yeasts, and mold fungi differ somewhat from higher plants and animals in their nutritional requirements for sulfur. While a number of microbial species are able to subsist on inorganic forms of sulfur, other species require biotin, thiamine, cystine, methionine, lipoic acid, the thiazole moiety, or other forms of sulfur for optimal growth. The sulfur requirement is a function of the microbial species or strain as well as of environmental conditions, including temperature, hydrostatic pressure, and the presence of other nutrients or metabolites. For example, a good many microbes can get along without lipoic acid in nutrient media provided acetate is present. When cultivated at increased pressures or temperatures near the threshold of the tolerance of a microbial culture, its sulfur requirements are much more exacting than when cultivated at the optimal pressure or temperature. These observations are interpreted as meaning the synthetic capabilities of microbes are greatest when grown under optimal conditions.

Since most microorganisms, like higher plants and animals, contain cystine, methionine, glutathione, and certain other organic sulfur compounds, growth in the absence of such sulfur compounds indicates their synthesis. From his studies on *Aspergillus nidulans*, Hockenhull (1949) has postulated the following stepwise conversion of sulfate into cystine:

Sulfate → sulfite → sulfoxylate → thiosulfate →
serine thiosulfate (cysteine-S-sulfonate) → cysteine → cystine.

The synthesis of methionine by other microbes has been shown to follow a similar metabolic pathway as far as cysteine:

$$\text{Sulfate} \xrightarrow{(1)} \text{cysteine} \xrightarrow{(2)} \text{cystathione} \xrightarrow{(3)} \text{homocysteine} \xrightarrow{(4)} \text{methionine.}$$

Mutants vary in their ability to carry out stages (1), (2), (3), or (4), according to Young and Maw (1958). They relate that the wood-rotting fungus *Schizophyllum commune* synthesizes dimethyl sulfide and methanethiol or methyl mercaptan by the successive reduction and methylation of sulfate:

$$SO_4^{2-} \rightarrow SO_3^{2-} \rightarrow CH_3SO_3^- \rightarrow CH_3SO_2^- \rightarrow$$
$$(CH_3)_2SO_2 \rightarrow (CH_3)_2SO \rightarrow (CH_3)_2S \rightarrow CH_3SH$$

Other microbes have been shown to form methanethiol from the degradation of methionine. Cyst(e)ine is also metabolized by certain microbes with the formation of methanethiol.

Among the sulfur bacteria, both photosynthetic and chemosynthetic autotrophs are able to oxidize either elemental sulfur, hydrogen sulfide, thiosulfate, or sulfite to synthesize various inorganic and organic sulfur compounds. The names, habitats, and physiological characteristics of several such organisms are given by Schwartz (1958), who emphasizes their importance in geochemical processes. The versatile synthetic ability of sulfur bacteria has also been reviewed by Wiame (1958). The main transformation of sulfur catalyzed by microorganisms are shown schematically in Fig. 3. Volumes have been written on the intermediate reactions and governing conditions.

Heterotrophs as well as autotrophs convert a certain amount of the sulfur and carbon being metabolized into bacterial cell substance, largely proteinaceous materials. Despite their small size, as compared with higher plants and animals, the microbial biomass in soil and in the sea is appreciable, owing to their numerical abundance, widespread occurrence, and the rapidity with which they reproduce or grow. Based upon the standing crop of bacteria in soil and in the sea and their presumed rates of reproduction, it is estimated that the total amount of organic sulfur cycled annually through the bodies of bacteria and allied microbes may be of the order of 1–10% as much as the total amount of sulfur cycled annually through the bodies of all plants and animals combined. This generalization takes into account the fact that whereas the life expectancy of most microbes is of the order of hours or days, the life expectancy of higher plants and animals ranges from days to decades. Although the standing crop of higher organisms is larger than the standing crop of microbes, there may be tens or hundreds of times as many crops (cycles) of microbes in a given period of time. Virtually all kinds of plant and animal organic matter are susceptible to microbial utilization. There is a wide range in the efficiency of microbes in converting organic matter into microbial cell substance. An average of about one-third of the organic carbon assimilated by heterotrophic bacteria and fungi appears in their protoplasm. Nothing is known regarding their efficiency in the conversion of sulfur compounds. While the major role of microbes as geochemical agents may be as mineralizers of organic matter, they also contribute substantially to the formation of organic sulfur compounds.

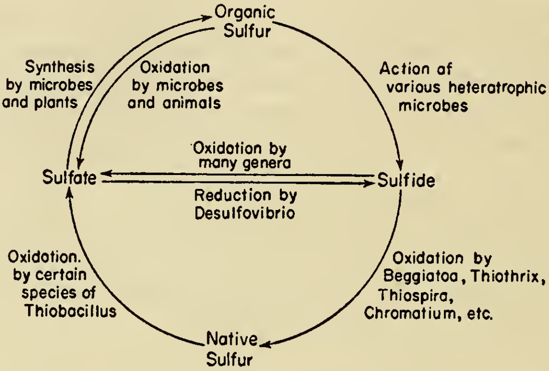

Organic Sulfur
Synthesis by microbes and plants
Oxidation by microbes and animals
Action of various heterotrophic microbes
Oxidation by many genera
Sulfate
Sulfide
Reduction by Desulfovibrio
Oxidation. by certain species of Thiobacillus
Oxidation by Beggiatoa, Thiothrix, Thiospira, Chromatium, etc.
Native Sulfur

FIG. 3. Salient features of the sulfur cycle in the biosphere.

As phrased by Abelson (1959), "Although annual production of organic matter is enormous, most of it is metabolized, mainly by microorganisms. Aerobic environments are particularly unfavorable for the preservation of organic chemicals. In the presence of oxygen and moisture, biochemical substances are rapidly consumed by microorganisms." Although less susceptible to attack under anaerobic conditions, organic materials are slowly decomposed even in the absence of free oxygen. Organic substances that escape microbial attack are subject to a variety of chemical hazards, including reactions with other materials. The intrinsic instability of most organic substances under natural conditions helps to account for the rapidity with which the constituent elements are cycled and for the general paucity of organic materials in ancient or fossil deposits. Speaking only of organic sulfur compounds, the principal exceptions are in fossil fuels to which reference has already been made.

Judging from their activation energy for degradation as well as from their occurrence in ancient sediments (Abelson, 1959), such non-sulfurous carbon compounds as porphyrins, the more complex lipids, and cellulose, for example, appear to be more stable than organic sulfur compounds synthesized by organisms. It seems significant that while alanine, aspartic acid, glutamic acid, glycine, leucine, phenylalanine, proline, and tyrosine have been found (Erdman *et al.*, 1956) in marine sediments, cystine and methionine are conspicuous by their absence. It is to be presumed that sulfurous amino acids occur in the proteins found in a variety of fossils referred to by Abelson (1959). However, no sulfurous amino acids appear among those mentioned by him as being present in fossils.

Conclusions

Sulfur is among the thirteen most abundant elements making up the crust of the earth, ranking fifth, sixth, and eighth in abundance in the whole earth, sea water, and living organisms, respectively. It occurs free and with other elements in thousands of combinations, a good many of which result either directly or indirectly from biochemical activities of bacteria, higher plants, and animals. Throughout the biosphere and hydrosphere, organisms modify juvenile forms of sulfur by promoting the weathering of rocks, altering its states of oxidation, and by catalyzing its combination with carbon, hydrogen, oxygen, and other elements. Organisms also play an important part in determining the forms of sulfur present in soil and marine sediments. Bacteria are believed to be responsible for large deposits of sedimentary sulfur, and they are known to fractionate isotopes of sulfur.

Among all forms of sulfur, sulfates and sulfides are quantitatively the most important that are modified by organisms. Both forms, in almost countless combinations, are formed, consumed, or otherwise altered by a great variety of organisms. Most bacteria and higher plants utilize inorganic sulfates in the synthesis of cyst(e)ine, methionine, and many other organic sulfur compounds essential for structural, physiological, or regulative purposes. Animals excrete both organic and inorganic sulfates. A major function of sulfate in geochemical cycles is as a carrier or reservoir of oxygen to provide for the oxidation of organic matter in anaerobic environments, a reaction catalyzed by sulfate-reducing bacteria. The latter liberate hydrogen sulfide and they may form free sulfur. Hydrogen sulfide is also formed from the degradation of sulfurous organic materials, and is a geochemical agent of the first order. As a reducing agent, it influences the oxidation states of iron and certain other elements. It also plays a role in pyrite and fossil formation, influences the preservation of organic matter in sediments, and combines with free oxygen, creating anaerobic conditions that may restrict biota. Some bacteria oxidize hydrogen sulfide as a source of energy.

Although bacteria and allied microorganisms are mainly mineralizers of organic matter, one must not overlook their importance as synthesizers of organic compounds. Besides the activities of chemosynthetic and photosynthetic microbes in the fixation of carbon dioxide, heterotrophs growing in the sea and soil convert an average of about 30% of the carbon content of assimilated compounds into microbial cell substance. Since nearly all kinds of organic matter are susceptible to microbial attack, enormous quantities are cycled through microbial cells, most of which contain from 0.1 to 1% sulfur. The susceptibility of the organic remains of plants and animals to microbial attack in the biosphere helps to account for the general paucity of such organic matter in fossils. Sulfurous organic compounds found in organisms seem to be more susceptible to decomposition than are corresponding non-sulfurous compounds.

Bacteria, higher plants, and animals synthesize hundreds of organic sulfur compounds, including amino acids, peptides, proteins, enzymes, vitamins, antibiotics, thiols, thiophene derivatives, thiocyanates, ethereal sulfates, etc. A good many of these sulfur compounds are optically active. Reference is made to some of the metabolic pathways by which such sulfur compounds are formed or modified by organisms.

Organisms of all kinds influence the state of sulfur and its combinations with other elements, notably carbon, oxygen, hydrogen, and iron. Man's influence as a geochemical agent is probably not as great as that of other classes or organisms. Man and all other organisms combined do not move as much sulfur as wind and water movements, although, by influencing its state, man and other organisms have a pronounced indirect effect on the transportation of sulfur. It is estimated that from 1 to 10% as much sulfur is cycled annually by bacteria and allied microorganisms as by all other higher plants and animals combined.

An attempt has been made to integrate a little of the extensive knowledge about sulfur and its compounds from the works of biochemists, geochemists, geologists, microbiologists, and mineralogists. Further cross-fertilization among these and related diciplines in future research can be expected to contribute substantially to many of the unsolved problems concerning sulfur and its compounds.

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CHAPTER 14

ORGANIC GEOCHEMISTRY OF SILICA *

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THE geochemistry of silica has been a prime target for research for many years because of its ubiquity in both surficial and deep seated rocks, and because of the complexity of physico-chemical and biochemical systems involving SiO_2 as one component. Difficulties in understanding and characterizing the chemistry of silica arise from three major characteristics of the compound SiO_2: (1) the polymorphism of crystalline and amorphous varieties of the solid; (2) the complex nature of molecular and ionic species in true solution and their distinction from colloidal species; and (3) the as yet incompletely known nature of and reactions between colloidal particles in suspension in aqueous media. Although the various forms of solid silica have been fairly well known and adequately described for the past several decades (Sosman, 1927), only recently (see summary by Iler, 1955) have chemists been able to elucidate clearly the nature of aqueous solutions, colloidal sols and gels, and the kinds of silica and silicate particles participating in solutions.

Silica solids—The essential facts of the crystal chemistry of solid silica are that there are several crystalline polymorphs, α-quartz (stable up to 573°C), β-quartz (573°–870°C), tridymite (870°–1470°C), cristobalite (1470°–1710°C), and the more recently discovered coesite, a high pressure modification (Coes, 1953). Of these, only α-quartz is chemically stable at room temperatures and pressures, although some of the others may persist metastably below their high temperature or pressure stability fields.

Amorphous silica is a disordered association of cristobalite crystallites only a few angstroms in diameter (Warren and Biscoe, 1938). As this size crystallite is little larger than one unit cell of cristobalite, the aggregate cannot properly be called cristobalite and, for almost every chemical purpose, can be considered as truly amorphous. The amorphous form of silica is metastable at room temperatures and may persist in sedimentary rocks for geologically significant times. Although there are many different kinds of amorphous silica gels, powders and glasses, they all have much the same ultrafine structure as revealed by X-ray diffraction. The different varieties are distinguished chiefly by the manner of aggregation of the colloidal particles, the amount of water held in the micelles, and the nature and amount of impurities. Opal is a geologically occurring variety of amorphous silica that is more or less hydrated and may contain minor impurities that impart distinctive colors to the otherwise transparent, colorless solid. Chalcedony, the major constituent of chert, a siliceous sedimentary rock, is mainly microcrystalline quartz containing various amounts of intergranular water, but may have an admixture of some amorphous silica (Pelto, 1956).

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* Chapter submitted in 1959.

All biogenically precipitated silica is amorphous, or opaline, silica. A great number of plants and animals, including diatoms, radiolaria, sponges, horsetails, bamboo and many other tropical plants, secrete silica. Regardless of the external form that the secretions may take, from the gelatinous tabashir found in bamboo to the sharp spikelike projections at the tips of stinging nettles, they are all amorphous silica and have roughly the same chemical properties. Diatom and radiolarian tests and sponge spicules are geologically important both as fossil remains and as sources of secondarily redistributed silica in sediments. The importance of many tropical plants as silica accumulators has been stressed by Lovering (1958).

Silica–water system—The silica–water system at room temperature has been summarized by Iler (1955). Amorphous silica dissolves to give

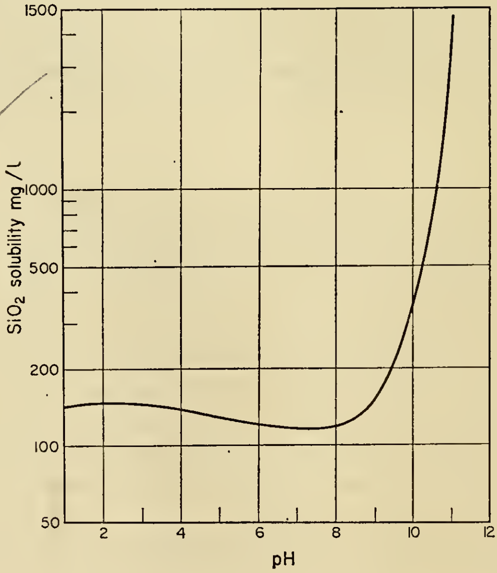

FIG. 1. Variation of solubility of amorphous silica with pH (after Alexander *et al.*, 1954).

monomeric silicic acid (H_4SiO_4) in true solution at pH values below 9. As crystalline quartz is the only stable silica solid at room temperature, any equilibrium between amorphous silica and water is a metastable one. This metastable equilibrium solubility of amorphous silica as H_4SiO_4 is around 140 mg/l. SiO_2, and is independent of pH (Alexander *et al.*, 1954). At pH values above 9, the molecularly dissolved H_4SiO_4 dissociates to give $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ ions; the monomeric form, H_4SiO_4, polymerizes to give subcolloidal or colloidal size molecules and, as a result, the solubility increases greatly (Fig. 1). Thus, the total solubility of silica is a combination of non-pH dependent (below pH 9) molecularly dissolved monomer and pH-dependent (above pH 9) silicate ions and polymers. The first dissociation constant (for the formation of $H_3SiO_4^-$ ion) has been given by Roller and Ervin (1940) as $10^{-9.8}$, and the second dissociation constant (for the formation of $H_2SiO_4^{2-}$ ion) as 10^{-12}. These values show the very weak acidic character of a silicic acid solution.

The temperature dependence of the solubility of quartz and amorphous silica has been investigated by Kennedy (1950) and Iler (1955). Both solids show increasing solubility with increasing temperatures. The solubility of amorphous silica increases from about 140 mg/l. at 25°C to about 400 mg/l. (SiO_2) at 95°C. Quartz solubility has not yet been adequately investigated in the range of temperatures from 25°–140°C,* mainly because the solubilities are so low and the quartz dissolution is so sluggish. Kennedy's data above 140°C show a continuing increase in the solubility of both amorphous silica (silica glass) and quartz up to about 330°C, beyond which the change in solubility with increasing temperature depends on the pressure. The curve for quartz solubility in Fig. 2 has been drawn by interpolating between Kennedy's lowest temperature and the approximate solubility at 25°C, about 10 mg/l. (Siever, 1957).

The pressure dependence of quartz and amorphous silica solubilities at temperatures below 140°C has not been investigated and is poorly known. Kennedy's data at higher temperatures show that with increase in pressure the solubility rises, but the magnitude of the effect at temperatures below 140°C is probably much smaller than the increase in solubility tied to temperature increase. However, geologic and petrologic observations seem to indicate that the pressure of rock overburden has been responsible for some solution of quartz grains in sandstones (Waldschmidt, 1941; Heald, 1956; Siever, 1959).

Rates of solution of silica are very slow at room temperatures. Amorphous silica may take from 10 days to 6 months to reach equilibrium with distilled water, depending on the variety of solid or powder used, fused silica glass being the slowest. Quartz is much slower to dissolve. For example, a sample of washed, acid treated quartz, 200 × 300 mesh,

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* J. A. van Lier published in 1959 *The Solubility of Quartz*, Ph.D. thesis, Utrecht; this work reports careful determinations of quartz solubility at 60°, 70°, 80°, 90°, and 100°C that indicate that Kennedy's lowest temperature values are too low. Van Lier extrapolates to 25°C to get a value of 11 mg SiO_2/kg.

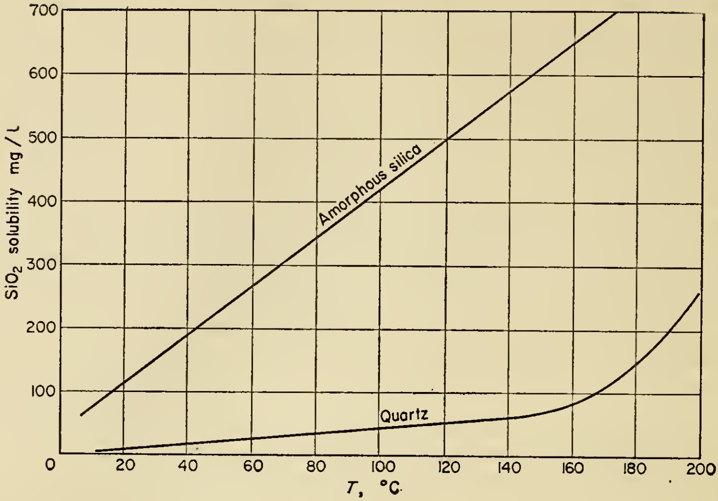

FIG. 2. Variation of silica solubility with temperature (after Kennedy, 1950 and Alexander *et al.*, 1954).

showed no appreciable solution in distilled water after two years. Very fine grained quartz powders (2–5μ), however, dissolve to reach equilibrium in the same period of time.

Colloidal silica—The formation of silica gel from a supersaturated solution is essentially a process of polymerization of H_4SiO_4 units with the splitting out of water molecules. The end result of this polymerization is a colloidal precipitate of SiO_2 in which all the water has been eliminated from the polymer, although water molecules may be retained as an adsorbate or in the open structure of the gel. Rates of polymerization are very much affected by pH. The slowest gel rates are in the acid (pH 2) and alkaline ranges (above pH 8), with the fastest gel time at around pH 5.5 (Iler, 1955). The gel rate increases with degree of supersaturation and varies with some impurities.

In aqueous solutions the colloidal precipitate is in equilibrium with about 140 mg/l. SiO_2 in true solution at pH values below 9. As pointed out above, at pH values above 9 the equilibria are more complex involving silicate ions and various dimers, trimers, etc. If equilibrium is attained, in the absence of biological activity, colloidal silica will not precipitate unless there is more silica in solution than the equilibrium amount. Similarly, a colloidal precipitate in contact with an undersaturated solution will dissolve until the solution reaches 140 mg/l. SiO_2 concentration.

In the laboratory at room temperature a precipitate of amorphous silica is always produced from supersaturated solutions rather than the stable solid, quartz. The conditions necessary at room temperature for the orderly polymerization of silicic acid or silicate ion units to form the spiral, densely packed structure of quartz have not yet been discovered, although quartz crystal synthesis at higher temperatures and pressures has been practised commercially for some years.

Geological evidence, however, shows that in nature both amorphous silica and quartz have been precipitated at low temperatures. The natural amorphous silicas are abundant and occur in a wide variety of geologic and biological conditions. The precipitation of quartz at low temperatures in natural situations has never been observed in surface waters, but the authigenic quartz found in many sedimentary rocks evidently formed at low temperatures for the rocks show no indication from the other minerals present of ever having been subjected to any great heat. The difference between the behavior in the laboratory and in nature may simply be the time factor. The precipitation of quartz at low temperatures is a very slow process.

Organic silicon compounds—Although there is a large body of chemical data on organic silicon compounds, including the silicic esters and the silicones, relatively few of them are of geological interest. So far as is known, no naturally occurring organic silicon compounds have been discovered in geological deposits. This may be attributed to the fact that the Si–O bond is very much more stable than the Si–C or HO–Si–C bonds and, in natural situations, the inorganic silicates will always form in preference to the silicones or silicic esters. In fact, even in silica secretions of modern plants it has not been shown that silicic esters or organosilicon compounds are involved (Rochow, 1951). However, some aspects of the organic chemistry of silicon and silica are of interest to geochemists, mainly those that relate to the ways in which silica is held and secreted by organisms.

Perhaps of greatest interest are reactions of silica with cellulose, for they may bear on the origin of silicified wood, discussed in more detail below. For some years there have been many commercial applications of the sorption of silica and sodium silicates by cellulose fibers (Vail, 1952). Merrill and Spencer (1950) performed experiments on the sorption of sodium silicate and silica sols by cellulose and came to the conclusion that a combination of van der Waals forces, hydrogen bonds, and chemical reactions with side groups of the cellulose molecule were responsible for the sorption, with different reactions being dominant for the silicate and the silica sols. Samec (1932) discovered that silica cannot be completely removed from natural celluloses even with strong reagents, and attributed this to covalent bonding between the silicic acids and alcoholic hydroxyl groups in cellulose. Merrill and Spencer also mention the possibility that silica may form very insoluble complexes with certain impurities such as aluminum, calcium or magnesium. A tentative explanation for the sorption of silicate ions on cellulose is the condensation of SiOH groups with the alcoholic hydroxyl groups of the cellulose.

Silica and silicic acid form complexes with different types of organic compounds such as catechol, some ethers and amides, triethyl phosphate, and tetraethylurea. Iler (1955) ascribes these complexes to the adsorption of the organic reagent on the surface of a highly branched polysilicic acid molecule. It is doubtful whether the association of hydrogen bonding polar organic molecules with silicic acids is of any great geologic interest for it has not been established that the organic compounds involved occur in natural environments. As we shall see below, it is also exceedingly unlikely that there are many natural environments in which polysilicic acid sols (or gels) can form.

In addition to forming organic complexes with silicic acids, silica, as a gel, is well known as an adsorbent for some organic materials, in particular, amines and long chain polar molecules. Many colloidal silicate structures, notably montmorillonite, serve as excellent adsorbers of organic materials (Grim, 1953). Ethylene glycol, for example, is used extensively as a material that enters into interlayer positions in montmorillonite to expand the lattice. Bernal (1951) used the affinity of organic adsorbates for colloidal silicates as a basis for speculation on the origin of primitive large organic molecules that were predecessors of living cells.

The important question of how silica is secreted and accumulated by organisms is still largely unanswered. Plants may accumulate silica as the residue from evaporation of silica rich fluids but, as Vail (1952) notes, the diatoms which secrete silica under water must use other unknown means. Iler (1955) suggests that these organisms produce insoluble aluminosilicates or magnesium silicates at the surface of the silica shell to protect it from dissolving in the sea water but this does not necessarily explain how the organism concentrates the silica in the first place. We can only speculate at the moment that there is some mechanism by which organic complexes with silica are formed transiently to concentrate the silica, and that following the concentration the organic complexes are broken up and the free silica is allowed to precipitate.

The silica cycle—The geochemical cycle of silica in the earth's crust has been elucidated by the study of silica and silicates in rocks, in conjunction with the chemical composition of the various kinds of waters, both surface and subsurface, that surround or percolate through them. We will start with that point in the cycle where siliceous rocks of metamorphic or igneous origin (formed under high pressure and temperature conditions) are exposed to subaerial weathering processes. In general, the silicate minerals of these rocks are unstable in the weathering environment and break down both chemically and mechanically. Much silica is released to solution during the decomposition of feldspars, amphiboles, pyroxenes, and micas. Quartz, being stable in earth surface environments and having very low solubility, is relatively untouched chemically, except for some slight solution, and is primarily mechanically degraded to finer sizes than the original crystals or crystalline fragments. The silica derived from the decomposition of silicate minerals is in true solution, primarily as H_4SiO_4, and is carried as such in rivers and near surface ground-waters; these waters have silica concentrations normally ranging from 5–25 mg/l. SiO_2, and thus are undersaturated with respect to amorphous silica. Though these solutions may be supersaturated with respect to quartz, the quartz–water system is so slow to come to equilibrium that no quartz is precipitated.

Not all of the silica is released, however; much of the original silica may be tied up in colloidal silicates, primarily the clay minerals, which are more or less stable in the weathering environment. For example, in the weathering of feldspar, first a mica is formed and then kaolinite (Sand, 1956; Garrels and Howard, 1957). In those areas where the ultimate in chemical weathering is reached, that is, in some tropical lateritic soils, the kaolinite is completely desilicated leaving behind gibbsite.

Another source of silica at the surface is hot springs water which, when suddenly cooled on reaching the surface, may precipitate amorphous silica leaving behind waters saturated with silica (140 mg/l.) (White *et al.*, 1956).

Eventually the silica contributed to solution by the weathering of siliceous minerals reaches the ocean. Sea water contains little silica in solution, rarely as much as 4 mg/l., and surface water usually contains less than 1 mg/l. It is obvious that the vast quantities of silica in solution contributed to the oceans by rivers must be precipitated in some way from sea water, or the sea would soon become saturated. The mechanism of precipitation is probably not inorganic, for sea water is not only undersaturated with respect to amorphous silica but also with respect to quartz. The solubility of silica is apparently unaffected by ionic strength, at least up to the ionic strength of sea water (Krauskopf, 1956; Greenberg and Price, 1957). We do know, however, that diatoms, radiolaria, sponges, and other organisms are very efficient extractors of silica from solution. It is probable that the oceans are kept undersaturated in silica (Siever, 1957) as a result of these biochemical mechanisms.

After burial, the sediments contain trapped sea water whose composition may gradually change. Amorphous silica shells of silica-secreters will gradually dissolve in the undersaturated waters. Thus, the concentration of silica in interstitial waters could conceivably rise to equilibrium values (140 mg/l.), although work on recent sediments (Emery and Rittenberg, 1952; Bruevich, 1953) indicates that the concentrations reached are only III about half this value. As a result of dissolution of biogenic silica, the interstitial water may reach concentrations such that they are supersaturated with respect to quartz and undersaturated with respect to amorphous silica; that is, they lie in the range 10–140 ppm SiO_2. In the long periods of time involved in diagenesis, the quartz–water system equilibrates and excess silica in solution crystallizes as quartz euhedra or overgrowths. Chert nodules probably formed from solutions locally supersaturated with respect to amorphous silica. The original gel formed gradually alters to chalcedony or microcrystalline quartz, the stable form.

As temperatures and pressures increase with deeper burial of the sediment, quartz becomes more soluble and this effect is shown by interpenetration of quartz grains showing sutured contacts in many sandstones. Large quantities of silica may be released to solution in this way; the solutions may then migrate to other rocks, if the permeability allows, or may be trapped in the pore spaces. If such a rock, with many unconnected pores, is then uplifted and reaches a lower temperature and lower pressure, the pore solution will then precipitate quartz in interstices or as overgrowths.

In the diagenetic environment, silica may also participate in chemical reactions to form altered or authigenically precipitated silicates. For example, tiny authigenic crystals of kaolinite and dickite have been noted frequently in sandstones; the interpretation usually given is that the crystals were precipitated from solution. Some may have been altered in the solid state from other silicates or phyllosilicates. Authigenic overgrowths of feldspar, tourmaline, and zircon are common in sedimentary rocks and are presumed to have been precipitated from solution.

If the sediment moves into a metamorphic environment as a result of increase in temperature or pressure, available silica in the sediment (quartz, clay minerals, etc.) becomes reorganized with other elements to form various suites of silicate minerals. Some rocks eventually may be incorporated into a melt, and silica then takes its part in the precipitation of igneous minerals from a cooling magma. These processes complete the silica cycle by reconstituting the original silicate minerals with which consideration of the cycle was started.

Silica in Modern Organisms

Only a few groups of invertebrate aquatic animals secrete silica as skeletal material. These include radiolarians, silicoflagellates, and certain sponges and foraminifers (Vinogradov, 1953). Most animal tissues contain at least minute amounts of silica, which may be in part in the form of organo-silica complexes. The presence in most animals of an excretory system probably is responsible for the non-accumulation of silica to the extent found in many plants. No essential role in the nutrition of higher animals has been demonstrated for silica (Iler, 1955).

Small amounts of silica are almost universally present in plants; however, except for diatoms, silicon is not usually regarded as one of the nutritionally essential trace elements. Differences of opinion about the essentiality of silicon in plant nutrition derive chiefly from difficulties in detecting and controlling the presence of small amounts of the element. Wooley (1957), using refined techniques, reported that if silicon is required in the nutrition of the tomato plant, it is in amounts less than 0.2 μg-atoms per gram dry weight of the plant.

Although silicon is not an essential element, several workers (see Iler, 1955) have found that increased amounts of silica produced favorable growth response in plants. At least two factors may be important in the beneficial effect: silica in solution in the soil increases the amount of phosphate ion available for uptake by the plant (Reifenberg and Buckwold, 1954), and silica within the plant may prevent toxic concentrations of other elements (Williams and Vlamis, 1957). Cooper and Hall (1955) suggested that in certain silica-accumulating grasses silicon has a significant passive role in enhancing the intake of CO_2 or CO_3^{2-} ions, thus contributing to high potential growth capacity. Resistance to fungal infection in certain plants has also been related to their silica content (Iler, 1955).

The plants most important in uptake of silica from both fresh and marine waters are the diatoms. These unicellular algae secrete siliceous frustules and resting spores from concentrations as low as 0.5 mg SiO_2 per liter (Lund, 1954) and, while alive, can prevent these structures from dissolving. Diatoms are responsible for the undersaturation with respect to silica of lake waters and, along with radiolarians and siliceous sponges, reduce the silica content of ocean waters. At least some species of diatoms can attack aluminosilicate minerals directly, obtaining silica from their decomposition (Hutchinson, 1957). Accumulations by diatoms, radiolarians, and siliceous sponges may figure in the formation of cherts and other siliceous rocks. Certain algae may have a minor role in the precipitation of silica from hot spring waters (Allen, 1934; White *et al.*, 1956).

Silica, chiefly in opaline form, is found in the tissues of many vascular plants. It occurs in various plant organs and in forms from diverse systematic groups (Netolitsky, 1929; Frison, 1948). Silica enters higher plants in the solutions taken up through the root hairs; there may be a relationship between high silica content of a species and low cation exchange capacity of its roots (Amos and Dadswell, 1948). Frey-Wyssling (1930) noted that silica deposits in most plants are located near the path of the transpiration stream, suggesting that they are eliminated as non-assimilable material. However, localization of silica in such plant parts as the barbs of nettles and the endocarps of palm fruits shows that silica may be more intimately involved in the plant chemistry.

Many monocotyledonous plants, especially grasses and cereals, have high silica contents. The hollow stems of bamboo may contain quantities of an unusual silica gel called tabashir, which is highly porous and includes organic solutes (Iler, 1955). The unusual amount of silica in *Equisetum* has been recognized in the use that furnished its common name, scouring rush.

Although coniferous woods typically are low in silica, some dicotyledonous woods contain appreciable amounts. Amos (1952) listed about 400 species of trees in which the oven dry weight of the wood included more than 0.5% silica; the maximum silica content reported was 6.4%. In general, wood from tropical and subtropical regions contains more silica than wood from temperate regions, and the resistance of certain tropical woods to attack by marine borers has been related to high silica content (Amos and Dadswell, 1948; Wangaard, 1956).

Large quantities of dissolved silica may be removed from the soil through uptake by silica-secreting plants. For example, cultivated sugar cane in the Hawaiian Islands accumulated 1720 lb of silica per acre in 2 years (Moir, 1936). This process may affect soil composition. Characteristic silica deposits from epidermal cells of grasses, termed phytoliths, may become part of the silica fraction of the soil (Smithson, 1958). Lovering (1958) suggested that uptake of silica by plants and subsequent removal of vegetal debris by erosion may be important in the development of laterites and other silica-poor soils. Russian authors (reviewed by Jacks, 1953) reported that lower plants, including certain blue-green algae, lichens, diatoms, and bacteria are effective in direct decomposition of silicate minerals in soils or rock.

Silica and biogenic deposits—The association of silica with biogenic deposits has been noted by many geologists and biologists. Among the most prominent of these are the diatomaceous and radiolarian oozes and their fossil counterparts, the diatomites and radiolarites. The siliceous oozes form at the bottom of the sea by the slow settling to the bottom of the silica-secreting planktonic organisms. Oozes of this type are documented in all of the oceans of the world as well as some freshwater lakes (Sverdrup *et al.*, 1942; Hutchinson, 1957). The abundance of the siliceous organisms seems to be related primarily to the amount of nutrients available and secondarily to the concentration of silica in solution. Vast increases in diatom populations follow volcanic ash falls which, as they alter and devitrify, liberate large quantities of silica to solution. Many ancient biogenic siliceous deposits, such as the Monterey Shale (Bramlette, 1946) and Arkansas novaculite (Goldstein and Reno, 1952; Goldstein and Hendricks, 1953), are associated with evidence of contemporaneous volcanism.

Perhaps the most common associations of silica with biogenic deposits are in chert and biogenic limestone. Chert is made up of chalcedony, which consists dominantly of microcrystalline quartz (Midgley, 1951; Folk and Weaver, 1952) and possibly amorphous silica (Correns and Nagelschmidt, 1933; Donnay, 1936; Pelto, 1956). The petrographic and geologic evidence is not conclusive, but suggests that most cherts were originally precipitates or gels of amorphous silica. This evidence includes the microcrystalline nature and included amorphous material of chert, the rhythmic banding found in many deposits and, more important, the fact that older cherts (Precambrian and Paleozoic) are clearly microcrystalline quartz from petrographic examination but younger cherts (Mesozoic and Cenozoic) may have much chalcedony (Pettijohn, 1957), i.e. contain more amorphous silica. In addition, most chert nodules show evidence of extensive compaction. Such compaction is compatible with origin as a low-density high water content gel and incompatible with a dense, low water content microcrystalline quartz precipitate. The geologic evidence supports the very early formation of chert nodules, in some cases as the replacement of primary carbonate precipitates.

A possible explanation for the occurrence of chert nodules formed in biogenic limestones ties in the presence of decaying organic matter with the nature of aqueous solutions in the early diagenetic interval immediately following the precipitation of carbonate. Correns (1950) suggested the increase in solubility of silica in alkaline solutions and the precipitation of carbonate in the same alkaline solutions and the inverse relationships of solubilities in acid solutions as the basic reason for chert precipitation. According to this view, in alkaline regions the silica always present in small amounts in a biogenic deposit would dissolve and carbonate would precipitate; in nearby acid regions the silica would precipitate and the carbonate would dissolve.

For such a mechanism to operate, however, the alkaline solutions necessary to dissolve silica would have to be at a pH of well over 9. In the sealed system calcite-distilled water, with vanishingly small pCO_2 the equilibrium pH is 9.98 (Garrels, 1960). This would be a possible natural situation in the lower parts of certain soil profiles, but would definitely not be applicable to a marine carbonate sediment. A marine sediment is precipitated in or near equilibrium with sea water, and the sea water–carbonate system is buffered with a pH not varying greatly from 7.5 to 8.5. The changes in interstitial water composition after burial normally result in lowering rather than raising of pH, probably as a result of the liberation of CO_2 from the decay of organic matter.

If the bottom bacterial population is such that decay of protein-rich organic matter results in the release of appreciable quantities of NH_3, however, then it is entirely possible for the interstitial waters to become so alkaline that a large amount of silica will go into solution. If the distribution of NH_3-producing decomposing organic matter is spotty, then diffusion gradients will be set up between the centers of decay and the surrounding mass of carbonate sediment. At the center of decay the waters will be alkaline, silica will dissolve, and carbonate will precipitate; silica will diffuse away from, and carbonate toward, this center. As the silica diffuses into the main mass it meets more acid solutions and precipitates as a gel. The carbonate-rich solutions will diffuse from the main mass to the center of decay and precipitate there, probably as clear calcite. The latter mechanism has been proposed by Weeks (1953) for the origin of calcareous concretions in some shales.

The above mechanism, or one like it, would result in the gradual dissolution and redistribution of biogenic silica (diatom and radiolarian tests, sponge spicules, etc.) and fine grains of terrigenous quartz from a general uniform distribution in the sediment to a discontinuous distribution as nodules or concretions. Although much of this proposed mechanism is hypothetical, the general outlines are valid in the sense that there must be some way, probably biochemical, whereby the interstitial waters become very alkaline. If the pH never rises above 9 anywhere in the sediment, then spicules and diatom tests will dissolve only until equilibrium solubility is reached and no gel will precipitate.

Thus, it is quite probable that, although there may be no organosilicon compounds formed, yet organic matter is indirectly responsible for the formation of chert. That some such mechanism operates is suggested by the association of organic matter with chert in some well known plant fossil-bearing cherts such as the Rhynie of Scotland. Another, more recently described organic-rich chert is the Precambrian Gunflint formation (Tyler and Barghoorn, 1954).

Another association of silica and organic matter is found in the uranium deposits of the Colorado Plateau province. Organic deposits of various kinds, chemically similar to coal extracts in many ways and interpreted as the products of alkaline extraction of coal and lignite beds (Breger *et al.*, 1955) occur with the uranium that is thought to have been originally carried in alkaline solutions (McKelvey *et al.*, 1955). Associated with these extracts and uranium is the redistribution of earlier extensive secondary silica cement in some of the sandstones of the Morrison Formation (Weeks, 1953). The alkaline solutions that extracted much organic matter and carried uranium presumably also had high concentrations of dissolved silica. The lowering of pH involved in the precipitation of organic matter and associated uranium also would precipitate the soluble silica.

Silicification of Biogenic Materials

Silica is an important geological agent for the preservation of animals and plants. Siliceous fossils range from structureless casts to petrifactions retaining minute anatomical details. In addition, original hard parts of silica-secreting organisms readily become fossils.

The hard parts of various invertebrates, e.g. foraminifers, ammonites, brachiopods, and corals may be replaced by silica. Often this replacement is exact enough to reproduce original layered structure and crystal orientation. Silicified bones of vertebrates are uncommon, though silica may fill cavities within the bone (Rogers, 1924). Silicified remains whose bodies were entirely organic are rare; silicified Miocene insects and other arthropods retaining detailed internal and external anatomical features are found in the Mojave Desert, California (Palmer, 1957) and illustrate this unusual type of preservation (Fig. 6).

Silicified plant fossils include preservational types comparable to those found in animals. The calcareous remains of charophytes and other algae may be replaced by silica. Fossil plants with structure and original organic material retained by silicification are much commoner than similarly preserved animals. Silicified wood is probably the most abundant material of this type.

Silica solutions involved in fossilization originate from the dissolution of silica and silicates through weathering, and less commonly, from volcanic hot springs. Silica deposited during life in the tissues of some vascular plants is not usually a factor in their silicification; however, silica secreted during growth was reported by Elias (1942) to be responsible for preservation of Tertiary grass fruits from the High Plains of United States. The common occurrence of silicified wood in materials of volcanic origin points to volcanic ash as an important source of silica for petrification.

This relationship led Murata (1940) to suggest that silicified wood in sedimentary deposits may indicate the presence of volcanic materials. Siliceous hot springs apparently mineralized the plants of Devonian age from the Rhynie Chert in Scotland (Kidston and Lang, 1921). The SiO_2 found replacing invertebrate remains in marine environments probably originated in part from dissolution of biogenically precipitated silica.

The silica in petrifications may be in either the amorphous or crystalline state. Although some crystalline silica may be present, chalcedony and opal predominate in Tertiary fossils. There is a tendency, which may be influenced by external conditions, for amorphous silica to assume the more stable crystalline state in the course of time. Consequently, much Mesozoic and older fossil material contains only crystalline silica. Silica crystals may be oriented with the wood structure or may be independent of it (Figs. 4, 5).

It is a common misconception that silicification of wood and other plant materials involves a molecule for molecule replacement of the original organic matter by the silica. Arnold (1941) pointed out the unlikelihood of such an exchange on the basis of the dissimilarity of the molecules involved. Retention of organic material within silicified wood has been shown both by analysis (Stromer *et al.*, 1933) and by removal of silica with hydrofluoric acid. After desilicification Arnold (1941) was able to embed Devonian wood and section it on a microtone. Light colored fossil woods with structure but no apparent organic material may have lost the organic constituents present during initial silicification through subsequent leaching and degradation.

Despite much discussion regarding the silicification of plant materials (e.g. Felix, 1897; St. John, 1927; Stromer *et al.*, 1933; Müller-Stoll, 1951; Schönfeld, 1955) no entirely satisfactory explanation of the process yet exists, and silicification of wood has not been achieved in the laboratory. The problem involves the complexities of plant cell wall structure and degradative sequences, silica chemistry and, quite probably, extended periods of time.

The cell wall in most woody plant tissues includes a thin primary wall and a thick, usually three-layered secondary wall. Each wall layer is composed of an oriented matrix of coalesced cellulosic microfibrils penetrated by a continuous system of interconnected microcapillary spaces that may contain lignin (Bailey, 1939). Orientation of the microfibrils differs in successive wall layers. Either the lignin or the cellulose may be removed from heavily lignified cell walls leaving a structurally intact residue.

Degradation of plant cell walls in nature occurs in a definite sequence both with regard to the components of the cell wall and to its lamellar organization. There is a reduction of original cellulose, leaving the more resistant lignin residue. The middle and inner layers comprising the bulk of the secondary wall degrade before the thin outermost layer of the secondary wall and the thin primary wall (Barghoorn, 1952).

Silicification entails the infiltration of silica in solution into the walls and lumens of more or less degraded plant material. A means for intimate penetration of siliceous solutions into the cell wall without any necessity for "replacement" of organic molecules is provided by microstructure of the wall. The silica may occupy the microfibrillar spaces created by removal of original cellulose in partially degraded woods or, in the case of unlignified primary tissues sometimes present in silicified bog material, possibly occupies the intercapillary spaces. Orientation of silica in relationship to the microstructure of wood has been shown with both the electron (Eicke, 1954) and light microscopes (Müller-Stoll, 1951).

Organic detritus derived from the degraded middle and inner layers of the secondary cell wall sometimes is extruded to the center of the lumen during silicification, suggesting that deposition began in the cell wall and proceeded into the lumen (Fig. 4). However, in wood immersed in siliceous hot springs in Yellowstone Park, Wyoming (Allen and Day, 1935) the lumens were filled with silica without silicification of the cell walls. Within a single specimen of fossil wood, the silica in the lumens and in adjacent cell wall layers may differ in orientation and crystal form (Müller-Stoll, 1951) (Fig. 3). Some kinds of tissues consistently are better preserved than others within the same specimen, reflecting the varying resistance of their cell walls to degradation. Structural preservation of animals by silica is rare because their tissues usually lack resistant cell walls.

Conditions causing precipitation of silica within biogenic materials are not understood. Silicification may take place in environments ranging from hot springs to marine sediments; thus it is unlikely that either temperature or initial concentration of silica is critical within rather broad limits. Silicification has occurred in plant tissues ranging from those virtually intact to lignitized wood (Schönfeld, 1955) and coal (Hoehne, 1954); degree of degradation and, consequently, chemical composition of the organic matter apparently is not a controlling factor. Natural waters contain both silica in true solution and lesser but varying amounts of colloidal silica (Krauskopf, 1956); hence, composition of the mineral solution is not necessarily constant.

Factors possibly affecting the silicification process may include pH changes ensuing from alteration of the organic material, influence of organic molecules and molecular aggregates upon colloidal silica, and alternate wetting and drying. Silica-bearing ground waters in areas where volcanic ash is common are commonly alkaline but have pH values less than 9. Encountering lower pH values within decaying organic matter might affect stability of silica solutions. Wetzel (1957) attributed the selective silicification of certain marine invertebrates to the presence of organic matter in them during diagenesis of the sediments. In terrestrial situations, alternate wetting and drying resulting from periodic rainfall or fluctuations in water table level could affect concentration of silica in solution and lead to precipitation.

Some reactions of silica solutions are extremely slow (Krauskopf, 1956);

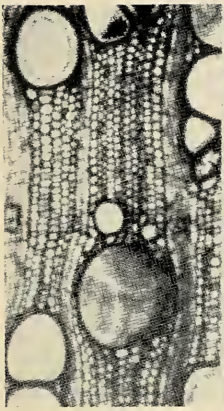

Fig. 3.

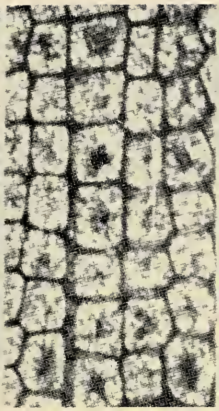

Fig. 4.

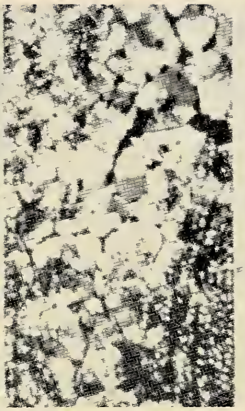

Fig. 5.

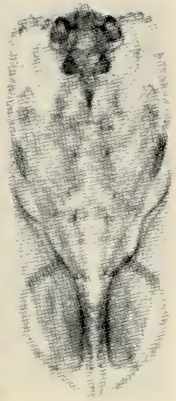

Fig. 6.

Fig. 3. Dicotyledonous wood, Eocene, × 50. Cell walls only slightly degraded. Silica in the large vessels is zonate (lower center) or follows the contour of the vessel (upper left).

Fig. 4. *Lepidodendron johnsonii* Arnold. Pennsylvanian, × 50 (polarized light). Silica has recrystallized within boundaries formed by the cell walls. Dark masses in the centers of the lumens are organic detritus derived from the secondary wall layers.

Fig. 5. *Araucarioxylon arizonicum* Knowlton. Triassic, × 50 (polarized light). Recrystallization of silica has disrupted cellular organization.

Fig. 6. *Dasyhelea australis antiqua* Palmer, × 50. This insect specimen is an unhatched female in pupa. (Original Pl. 34, Fig. 12, *U.S. Geological Survey Prof. Paper* 294–6. Photo by courtesy of A. R. Palmer.)

time beyond that available in ordinary experimental work may well be required for the silicification process. This possibility is supported by the fact that the youngest truly silicified wood known to the writers is of early Pleistocene age.

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CHAPTER 15

BIOGEOCHEMICAL ASPECTS OF THE FORMATION OF MARINE CARBONATES*

by MILTON WILLIAMS† and ELSO S. BARGHOORN‡

FROM the standpoint of sedimentary geology, one of the most important problems in geochemistry is that of the precipitation of marine carbonates. For the purposes of this discussion, the problem may be defined as that of providing the explanation of why, how, and under what circumstances carbonates precipitate, where in marine waters precipitation occurs, and in what form and in what amounts carbonates are formed in particular environments. Eliminated by this definition are the grosser aspects of transport and accretion after formation and of later diagenesis in carbonate sediments.

Consideration of the problem presented by carbonate deposition on the vast scale in which it occurs in warm shallow seas leads to the realization that there are many gaps in our knowledge with regard to both geological aspects and geochemical mechanisms. In treating the problem in the past, and in current thinking as well, two concepts have been proposed, drawn from a wide range of observational data. These concepts involve on the one hand solar evaporation of sea water with concomitant inorganic precipitation (Smith, 1940; Illing, 1954; Cloud, 1955), and on the other hand a group of varied biological processes effected by plants, animals, and microorganisms (Drew, 1914; Bavendamm, 1932; van Overbeek and Crist, 1947; Lowenstam and Epstein, 1957). A comprehensive review of the subject has been made by Revelle and Fairbridge (1957). Even a cursory survey of the literature reveals a wide divergence of opinion as to the relative effectiveness of these various factors and shows also that the proposed mechanisms are largely undefined in quantitative terms.

Several years ago, during the course of a search for a plausible explanation of the mechanism of carbonate precipitation, a working hypothesis was evolved. Although this hypothesis was directed specifically to the problem of recent carbonates which are forming today, it is likewise applicable to the problem of precipitation of carbonate deposits in the past.

First, it was assumed that purely inorganic precipitation of marine carbonates by solar evaporation of sea water, without the intervention of biotic processes, is rare in nature today and cannot be of significance. This argument is based in part on an apparent absence or paucity of recent carbonates in some hypersaline waters (the Mediterranean Sea, for instance, is a conspicuous example of a large body of hypersaline water, yet it is not renowned as an area of extensive deposition of recent carbonates), and in part on lack of evidence of hypersalinity in some areas in which lime muds are being deposited (such as the Gulf of Batabanó in Cuba and the Florida reef tract).

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Second, it was assumed that virtually all marine carbonates are precipitated directly or indirectly as a result of biological processes in marine waters—some carbonates within the organism, in the form of discrete and usually characteristic skeletal structures—and some external to the organism as a result of chemical change in sea water in the immediate vicinity induced by photosynthesis. In the case of plants, this mechanism is visualized as the process of extraction of carbon dioxide from the ambient water by photosynthetic organisms, with resulting shift in the equilibrium of the carbon dioxide–bicarbonate–carbonate system in the direction of carbonate precipitation. The rate at which carbon dioxide is abstracted by the process of photosynthesis during the diurnal peak of activity is usually far in excess of the rate of restitution of carbon dioxide in the sea water by diffusion from the atmosphere. Even though part of the carbon dioxide deficiency is restored temporarily by respiration of the organisms, the net effect in areas in which plankton and benthonic plant life are abundant is the precipitation of carbonate ion as calcium carbonate.

The precipitation of carbonates as a result of photosynthetic activity has been proposed by various workers (Davis, 1900; Craig, 1953), though virtually no field or laboratory evidence has been offered in support. In this connection, one of the writers (ESB) some years ago collaborated with the late Frederick S. Hammett in making a large number of observations of diurnal variations of pH in shallow open water of Massachusetts Bay over a period of several summer months and related these to the photosynthetic activity of phytoplankton within the bay. During hours of intense illumination by sunlight, it was found that the pH increased markedly to values as high as 8.52, and, during the dark, respiration of the plankton resulted in a sharp decrease of the pH to values as low as 7.82. The amplitude of the diurnal shift in pH was directly correlated with the duration and intensity of daily insolation. The likelihood of photosynthesis being an important factor in carbonate precipitation has likewise been further strengthened by unpublished observations of W. A. Collier of the Fish and Wildlife Service, who has shown that continued intense artificial illumination of marine aquaria leads to an increase of pH to values in the range of from 9 to 10, and to the precipitation of significant amounts of calcium carbonate. No evaporation was involved in this precipitation.

At this stage in the formulation of the hypothesis, a tentative but incomplete answer had been framed for the question of why and how carbonates precipitate. The line of reasoning which had been followed also suggested clues to where in the seas carbonates might be expected to be formed.

If the precipitation of marine carbonates is indeed due directly or even indirectly to vital processes, then the logical sites of formation are in those areas in which photosynthesis is at a relatively sustained high level. Such areas must meet several requirements which have been well established by marine biology. First, there must be relatively intense illumination within the euphotic zone. This condition, in turn, dictates not only that the area must lie in a moderately low latitude but also that the water must be reasonably free of silt. Second, the water temperature must be sufficiently high to favor rapid metabolic activity. From the literature of marine biology (Ekman, 1953), it is apparent that these favorable conditions of illumination and temperature are met largely, if not only, between the latitudes of 30° N and 30° S.

A third requirement for abundant photosynthetic activity is a sufficient supply of inorganic nutrients for growth. The major nutrients which ordinarily limit productivity are nitrogen and phosphorus. Actually, within the boundaries in the oceans which are imposed by intensity of available sunlight and favorable temperature, it is the availability of these inorganic nutrients which governs the population and growth of organisms and their total productivity.

In view of the fact that these three requirements—illumination, temperature, and availability of nutrients—are necessary conditions for the support of abundant life in the oceans and thus may be assumed to be necessary for the precipitation of carbonates, the question then arises as to where and under what circumstances these requirements are most favorably met. Some evidence on this point is furnished by the distribution in the oceans and seas of living coral reefs, which thrive only where phytoplankton is plentiful. It is well known that, in general, coral reefs occur only on the western sides of the ocean basins, usually close to land masses. This distribution suggests that the source of the necessary nutrients may be related to upwelling of deep oceanic waters, carrying nutrients dissolved from bottom sediments or released through microbial activity in the deeper parts of the oceans. Such upwelling may exist as a consequence of Coriolis currents causing a pile-up of water against the land masses forming the western boundaries of the ocean basins. Although the general concept of upwelling as a result of Coriolis currents can be called upon to explain the presence of coral reefs on the western sides of the ocean basins, it is obvious that additional information is necessary for the elucidation of the specific locations both of reefs and of areas of precipitation of other forms of carbonates.

In order to explore the factors which might pinpoint these areas, attention was given to a particular region in which recent carbonates are abundant—the so-called American Mediterranean (i.e. the Caribbean and Gulf of Mexico region)—in the hope that carbonate occurrence might be related to physiographic features and to water currents.

The region is illustrated in Fig. 1, together with major water currents and the more important known occurrences of recent carbonate accumulations. These accumulations consist, in most cases, of both coral reefs and lime muds. Although the interrelationship of reefal carbonates and of lime muds is an important and interesting part of the carbonate problem, attention can be given in this brief discussion only to the broader regional aspects of carbonate formation.

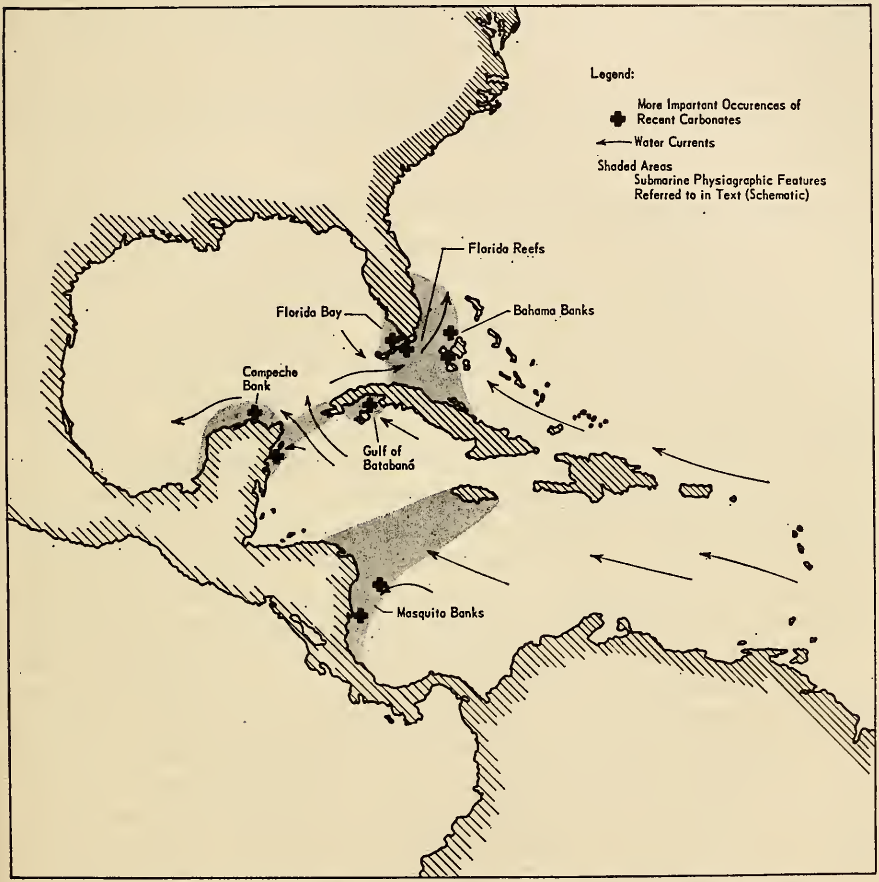

FIG. 1. Distribution of recent carbonates in the American Mediterranean.

Inspection of Fig. 1 reveals an interesting relationship. Each of the areas of carbonate deposition is down-current from a rise or sill on the ocean floor or from a strait. In the case of the Bahama Banks, the Florida current traverses the Florida Strait and passes over a sill before mingling with the Antillean current and overriding the Bahama Banks. In the case of the Mosquito Banks, a portion of the water flowing through the Caribbean passes over a part of the Jamaica Rise, then turns southward to flow over the Mosquito Banks. Water flowing over the Campeche Bank has both traversed the Yucatan Strait and passed over the Yucatan Sill. The Florida reefs are exposed to a countercurrent of the Florida current after the latter has flowed through the Florida Straits and over the Florida Sill, and even the northern part of the Bay of Florida receives water from the countercurrent. Water in the Gulf of Batabanó passes over a sill or threshold at the southeastern entrance to the Gulf.

Is there, then, a possibility that deeper waters are brought to the surface by disturbances accompanying flow over a sill or rise or through a strait, and, if so, does this exert control over the occurrence of carbonates? From the standpoint of physical oceanography, the writers know of no evidence of upwelling or of divergences in the areas where carbonates occur in the American Mediterranean, yet the occurrence of living reefs and the abundance of other forms of aquatic life necessitate a high phytoplankton population and rate of productivity.

In order to investigate the hypothesis that recent carbonates, particularly those of the American Mediterranean, are precipitated primarily as a result of vital processes, a series of studies of carbonates in the region was initiated. This has consisted to date of observations in the field in Florida Bay, in the Florida reef tract, and in the Gulf of Batabanó (work in the latter area was made possible by the kindness of Jersey Production Research Company of Tulsa), and of laboratory examination of carbonates from these areas and from the Bahama Banks.

Observations made in the Florida and Batabanó areas verified the existence of a diurnal change of pH. In Florida Bay, the pH of surface water ranged from a high of 8.9 in bright sunlight to a low of about 8.0 after dark. In Florida Bay and in the Florida reef tract, the principal organisms responsible for photosynthesis appeared to be phytoplankton (population estimated very crudely by means of a portable absorption spectrophotometer) and, perhaps even more important, the bottom-growing turtle grass, *Thalassia testudinum*. In the Gulf of Batabanó, in which the rate of carbonate formation seems to be appreciably less, there was very little diurnal change of pH of surface water, but a change of more than 0.5 pH unit was observed in the bottom water, close to the turtle grass, during the day. From the standpoint of the actual fixation of carbon in photosynthesis, the role of turtle grass is apparently much more important in this area than that of phytoplankton, which was present in rather low concentration.

Copious development of turtle grass was observed in all lime mud areas visited. Generally, the muds consisted of acicular crystals of calcium carbonate, with recognizable fragments of calcareous algae and of bryozoa. All of these forms were found as encrustations on the leaves of the turtle grass. Similar encrustations are found on herbarium specimens of species of *Thalassia* from the Red Sea, South China Sea, Coral Sea, and Caribbean, suggesting that photosynthetic activity of this plant is a very important factor in carbonate precipitation in shallow warm tropical seas in all parts of the world. Two characteristics of the plant are of interest—first, its habitat in marine waters to a maximum depth of about 60 ft, which may explain in part the fact that lime muds are predominantly found only in shallow waters, and, second, its deep growing subsurface stems and roots which are able to derive nutrients from fairly thick layers of sediment, so that nutrients may be cycled from grass to sediment after death of the plant, thence to living grass.

An idea of the magnitude of photosynthetic activity of *Thalassia* may be gained from measurements which have been made of the standing crop of the grass in Puerto Rican waters (Burkholder, 1959). The *dry weight* of the whole plant was found to range from 3.1 to 32.9 tons per acre. Similar measurements of the standing crop in Puerto Rican waters of the green alga *Halimeda*, also an important organism from the standpoint of photosynthesis, yielded values up to 43.3 tons dry weight per acre. Much of the weight of *Halimeda* is, of course, attributable to the calcium carbonate skeletal structure.

The role of photosynthetic activity in the precipitation of carbonates from sea water may be assessed by consideration of the relationship of the ionic constitution of sea water to pH. If, for example, it be assumed that normal sea water of pH 8.2 is initially saturated with respect to calcium carbonate, then, from the chemistry of the system (Sverdrup and others, 1949; Harvey, 1955; Monaghan, 1958) an increase in pH to 8.9 should result (assuming no supersaturation with respect to calcium carbonate after attainment of the higher pH and no dependence of solubility of calcium carbonate on pH) in the precipitation of about 35 mg of calcium carbonate from each liter of sea water. The amounts of calcium carbonate which may be precipitated by pH increases of the magnitude of those observed in Florida Bay and in the Gulf of Batabanó are much greater, incidentally, than the amount which might be released from solution by a reasonable extent of solar evaporation. This point may be illustrated by consideration of the amount of carbonate which might be precipitated as a result of isothermal evaporation of sea water in equilibrium with atmospheric carbon dioxide. If it be assumed that the sea water is initially saturated with respect to calcium carbonate and that there is negligible increase of solubility of calcium carbonate with increasing salinity, then the removal by evaporation of as large an amount as 10% of the water might be expected to result in the precipitation of perhaps 10 mg of calcium carbonate from each liter of the original sea water. It is thus apparent that increase of pH accompanying photosynthesis is a more potent agency in carbonate precipitation than removal of water by evaporation.

Though observations in the field indicated strongly that recent carbonates in the areas visited are formed as a result of biologic processes, additional evidence on their origin was sought by laboratory examination of the sediments. Among the various determinations made in the laboratory, possibly the most instructive were the carbon isotope ratios of the carbonates and of the dissolved carbon dioxide components in the sea waters associated with them. The isotopic compositions were determined by A. C. Daughtry and Douglas Perry of Humble Oil & Refining Company, Houston. The results of the measurements of the isotopic compositions are summarized in Fig. 2, in which the relative carbon 13/carbon 12 concentrations are shown in comparison with the present concentration of these isotopes in atmospheric carbon dioxide. Most of the data points are averages of determinations on numerous samples; in some cases these averages represent groups of widely divergent values.

Also shown in Fig. 2 are the relative isotopic concentrations of carbon in the components of the system

$$\begin{array}{c}\text{Atmospheric}\\ \text{carbon dioxide}\end{array} \rightleftharpoons \begin{array}{c}\text{Dissolved}\\ \text{bicarbonate}\end{array} \rightleftharpoons \begin{array}{c}\text{Solid calcium}\\ \text{carbonate}\end{array}$$

as predicted by theory for a system in isotopic equilibrium (Urey, 1947; McCrea, 1950). If carbonates were precipitated by such a simple process as solar evaporation of sea water, the carbon isotopic compositions both of solid carbonates and of dissolved bicarbonate might be expected to be essentially those predicted by this theory.

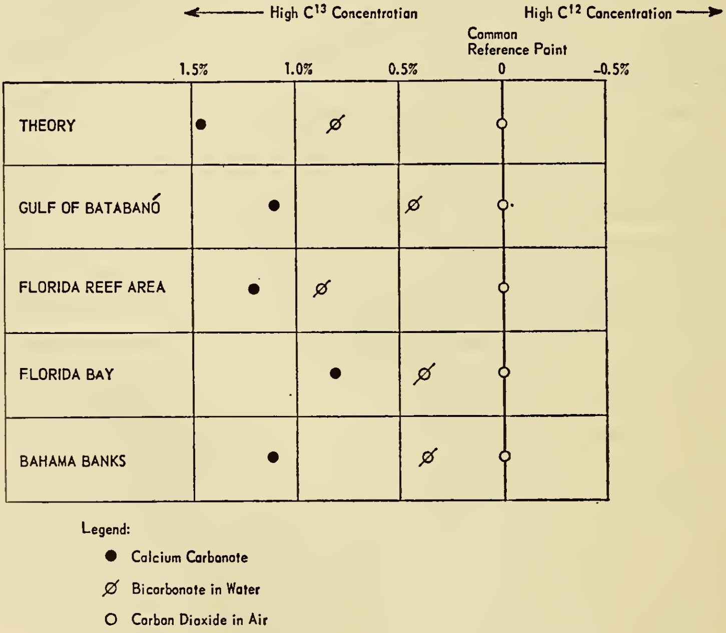

Fig. 2. Relative carbon isotope concentrations in the American Mediterranean.

It is quite apparent from Fig. 2 that the isotopic compositions of neither carbonate sediments nor dissolved bicarbonates coincide with the theoretical values. The carbonates contain less carbon-13 than required for equilibrium, and the dissolved bicarbonates generally also contain less.

A prominent feature of Fig. 2 is the extreme variation in carbon isotopic composition of the dissolved bicarbonates. This variation is real and in part is a reflection of fluctuations with time in isotopic composition of bicarbonate in waters from particular areas. Though this point has not been investigated in detail, it was observed that waters obtained from the Florida area at intervals of the order of months yielded radically different values. In view of the isotopic fractionation involved in photosynthesis (Craig, 1953; 1954) and of the dependence of the exceedingly complex cycle of carbon in the marine biosphere on illumination and temperature, it might be expected that the carbon isotopic composition of dissolved bicarbonate should, in waters of high productivity, exhibit seasonal and diurnal variations of cyclical nature.

The interpretation of isotopic data such as appear in Fig. 2 in terms of the probable mechanism responsible for precipitation of carbonates has been considered by Craig (1953) (see also a summary by Craig in Revelle and Fairbridge, 1957) and by Lowenstam and Epstein (1957). In the light of the researches of these authors, it appears that lack of carbon isotopic equilibrium and lack of constancy of the carbon isotopic compositions of carbonates are the rule, rather than the exception, in the case of marine carbonates of known biogenic origin. When interpreted against such a background, the data on the recent carbonates of Fig. 2 accordingly support the view that these carbonates were formed as a result of life processes in the sea.

In summary, it appears that biological phenomena or biological processes are the principal cause, directly or indirectly, of carbonate precipitation in the oceans and that the sites of precipitation bear recognizable, though complex, relationships to ocean currents and to physiographic features of the ocean basins.

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